HYDROLOGICAL AND MICROBIOLOGICAL RESEARCH IN SUPPORT OF AMD PREVENTION FOR WASTE ROCK AND TAILINGS

Final Report

IRAP Project No. 22643U

June 1994

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APPENDICES

1. INTRODUCTION

The overall objective of this project was to establish the chemical, biological and microbiological foundation for a technology which will prevent or curtail acid mine drainage from waste rock and tailings.

Four tasks were identified at the onset of the project with respect to the 'eco-layer':

1. Quantification of water distribution and flow properties in the zone between the surface and water table in columns with different treatment design.

2. Quantification of oxygen consumption inside different types of 'eco-layers'

3. Examination of bacterial activities and biofilm development on sulphide grain surfaces, caused by dissolution of NPR.

4. Analysis of precipitates chemistry and microbial consortia.

2. TECHNOLOGY DEVELOPMENT

As the details of objectives 1 and 2 were addressed, it became apparent, that the quantification of the flow properties and the oxygen consumption in the' eco-layer' was very complex in tailings columns. The tailings columns would always be prone to short circuiting and edge effects are strong. This would not yield meaningful results.

To produce data for the technology to apply to coal waste , columns with coal waste from Cape Breton Development Corporation (DEVCO) have been set up with different types of phosphate rock, Long Harbour Sand (LHS) from Newfoundland and Natural Phosphate Rock (NPR) from North Carolina. The set-up is shown in Plate 1. These

PLATE 1: DEVCO coal column expt.

columns have received water at regular intervals and the acid mine drainage has been collected. The conductivity, pH, Em, and acidity of the column effluent are summarized in Appendix 1.

The experiment is continuing, as it has to run to complete exhaustion of the acid generation from the coal waste. The LHS treatments are producing a very good improvement in the effluent characteristics.

The results from these column tests can be related to an ongoing field experiment were LHS is integrated into an test pile (5m x 5m and 3m in height) of coarse coal waste uncompacted at the Victoria Junction Coal Washing plant in Cape Breton from DEVCO (Appendix 2).

To address the functioning of the 'eco-layer' instead of quantification of flow and oxygen consumptions, it was further decided, together with industry, that a more pragmatic approach

be adopted. Plots with the 'eco-layer' on tailings sites should be set up directly in the field. Plots were set up on acidic old uranium tailings in Elliot lake (Stanrock, Denison Mines) and on fresh base metal tailings in Copper Cliff (Inco, Ltd). The application of a mixture of phosphate rock, organic matter and seed is referred to as a PHITO cover and acronym for Phosphate Heterotroph Inhibition of Tailings Oxidation. The set up of the plots was supported by Inco and Denison Mines.

The PHITO plots were set up in 1993 and are being monitored since then. In Plate 2 the plot on the Stanrock tailings is shown 2 months after set-up and in Plate 3 the plots on the Inco tailings are shown. Tailings samples have been collected and are awaiting analysis. Details of the application rates used and the plot lay out are given in Appendix 3 which comprises progress reports May 1993 and July 1993.

Plate 2: PHITO plot on old uranium tailings in Elliot Lake 2 months after installation.
Plate 3. PHITO plot on fresh base metal tailings in Copper Cliff 2 months after installation.

Objective 3 and 4, investigating the characteristics of the biofilm formed on waste rock and on coal was carried out in 1992, using scanning electron microscopy linked to EDX analysis in the Department of Biology, McMaster University. The findings were summarized in a progress report (April, 1993) attached as Appendix 2. The results gave clear indications that NPR application leads to the formation of a biofilm/secondary precipitate film covering the pyrite surface were correct.

The waste rock experiment had been set up prior to seeking support from NRC. With the results of the microscopy study at hand it was decided that the effluent from the waste rock drums should be monitored further, going through several winter and summer cycles. The data on pH, acidity, conductivity and Em are summarized for the waste rock effluent in Appendix 1.

3. TECHNOLOGY PROMOTION AND SALES

A feasibility study was carried out for Kennecott Copper to apply the technology to their waste rock pile and leach water. Recommendations were made to carry out field test. The client ordered sample material through Boojum from TexasGulf and set up their own tests.

A similar experience was encountered with Zeneca, which retained Boojum Research for a feasibility study of their Iron Mountain property with severe acid mine drainage conditions. Zeneca were also very interested in the technology and proceeded to order samples of the NPR from TexasGulf for testing through Boojum. It also became apparent from inquiries made by Zeneca with researchers which had initiated work on phosphate rock with coal wastes prior to the Boojum study, that the research work was discontinued due to undefined reasons.

In April 1994, the 3rd International Conference on Acid Mine Drainage Abatement took place at Pittsburgh. Summary sheets of the applications of the Natural phosphate rock in acid mine drainage inhibition were prepared for promotion of the technology. Together with Texasgulf

a booth was manned at the conference. The conference was attended by 1500 delegates, from 18 countries.

Their interest at the conference in the phosphate rock applications was very intense. As a result, Texasgulf is preparing a proposal to Boojum to market and promote the application of phosphate rock with Boojum Research supplying the service for the applications. If this comes to fruition, the market potential will be realized. A royalty agreement for sales of NRP has already been agreed to.

Boojum Research is presently seeking funding for the monitoring phase of the ongoing experiments through the MEND program. Unfortunately a decision in this joint industry government program is lengthy and might be hoped for in 1995. The proposal and the replay are given in Appendix 4. Further requests for funding have been made to ZENECA and are presently under consideration (enclosed in Appendix 4).

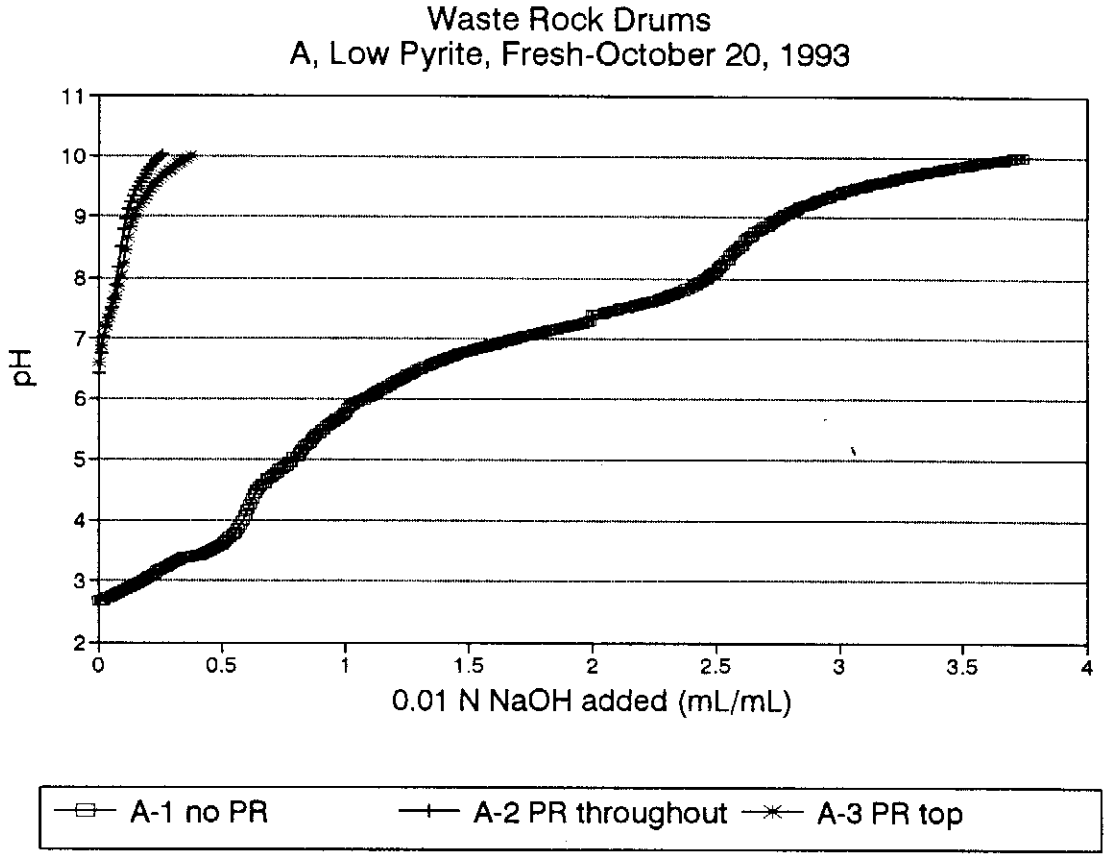
APPENDIX 1

EXPERIMENTAL DATA UPDATE

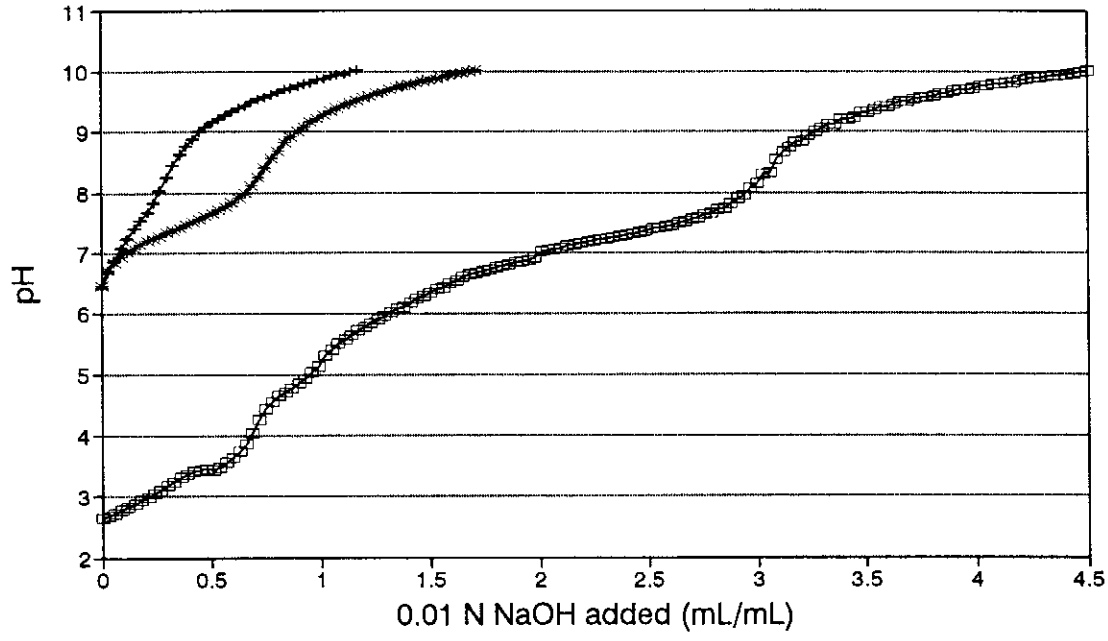
WASTE ROCK DRUMS

Table 1: Accumulated acidity after 678 days (to July 4, 1994)

Drum	Rock type	Treatment	Acidity (g)	Inhibition (%)
A1	low pyrite	control	62	
A2	fresh	+ PR mixed	3	95
A3		+ PR layer	4	94
B1	high pyrite	control	55	
B2	fresh	+ PR mixed	3	95
B3		+ PR layer	7	87
C1	low pyrite	control	166	
C2	>4 y weathering	+ PR mixed	12	93
C3		+ PR layer	33	80
E1	high pyrite	control	26	
E2	>4 y weathering	+ PR mixed	2	93
E3		+ PR layer	40	-52

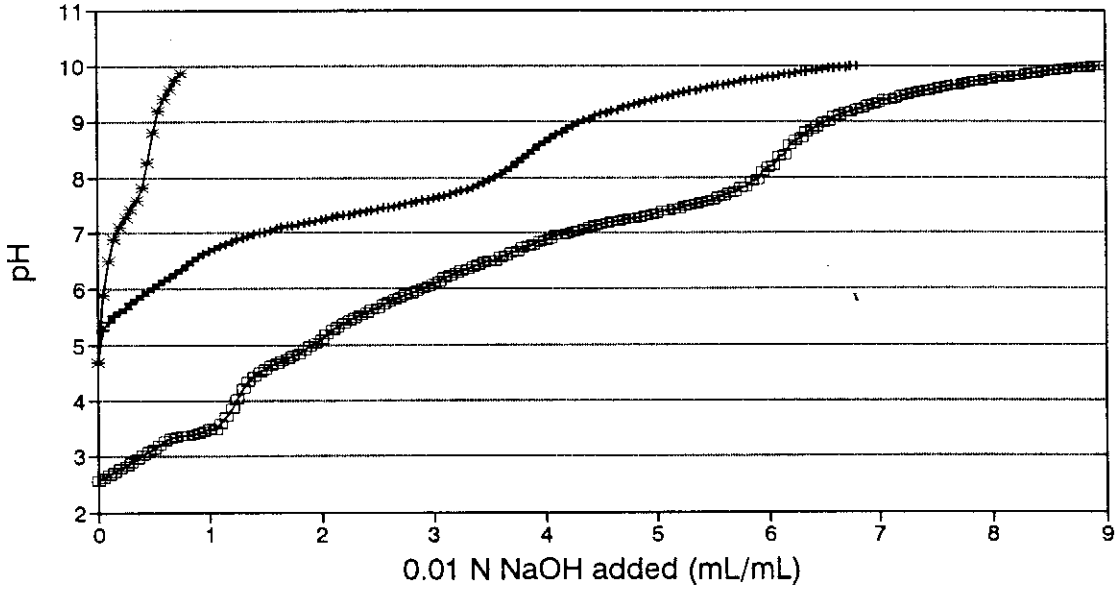


Waste Rock Drums
B, High Pyrite, Fresh-October 20, 1993



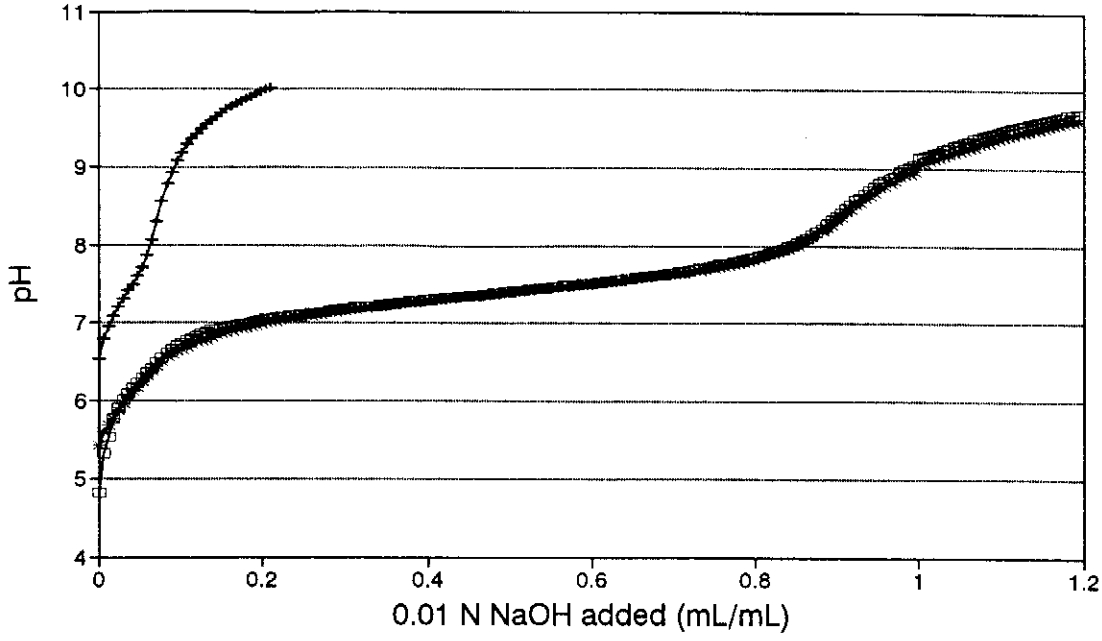
B-1 no PR B-2 PR throughout B-3 PR top

Waste Rock Drums
C,Low Pyrite, Weathered-October 20,1993

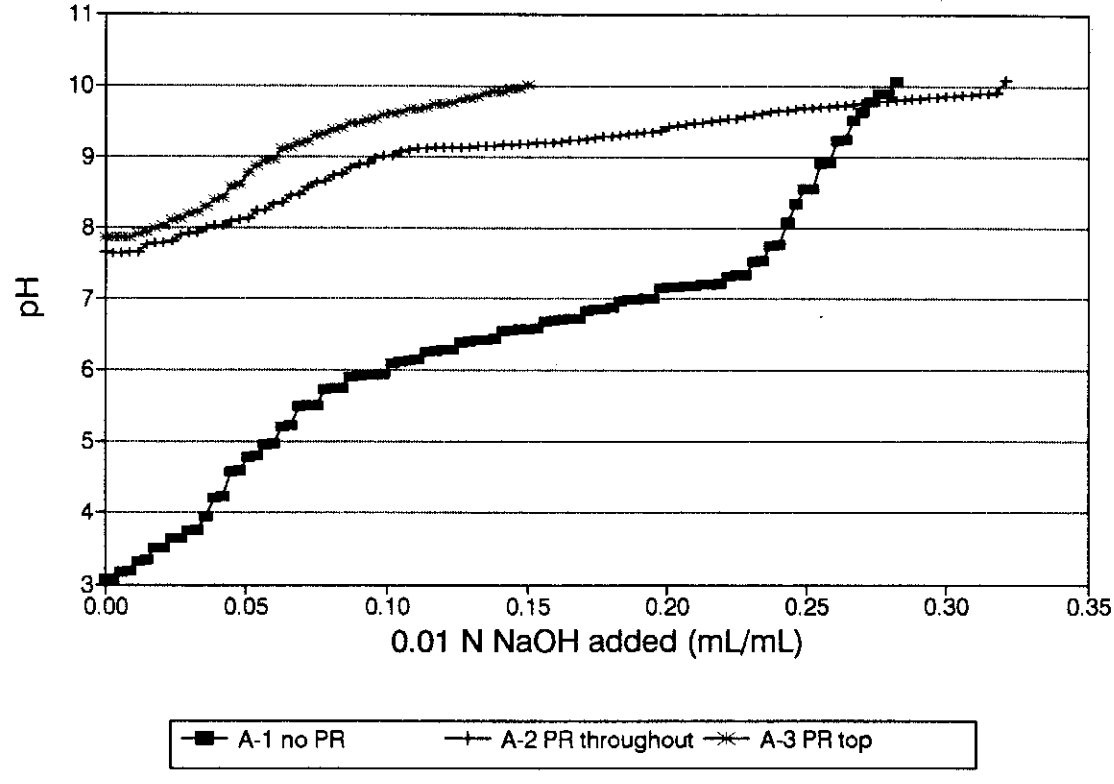


C-1 no PR C-2 PR throughout C-3 PR top

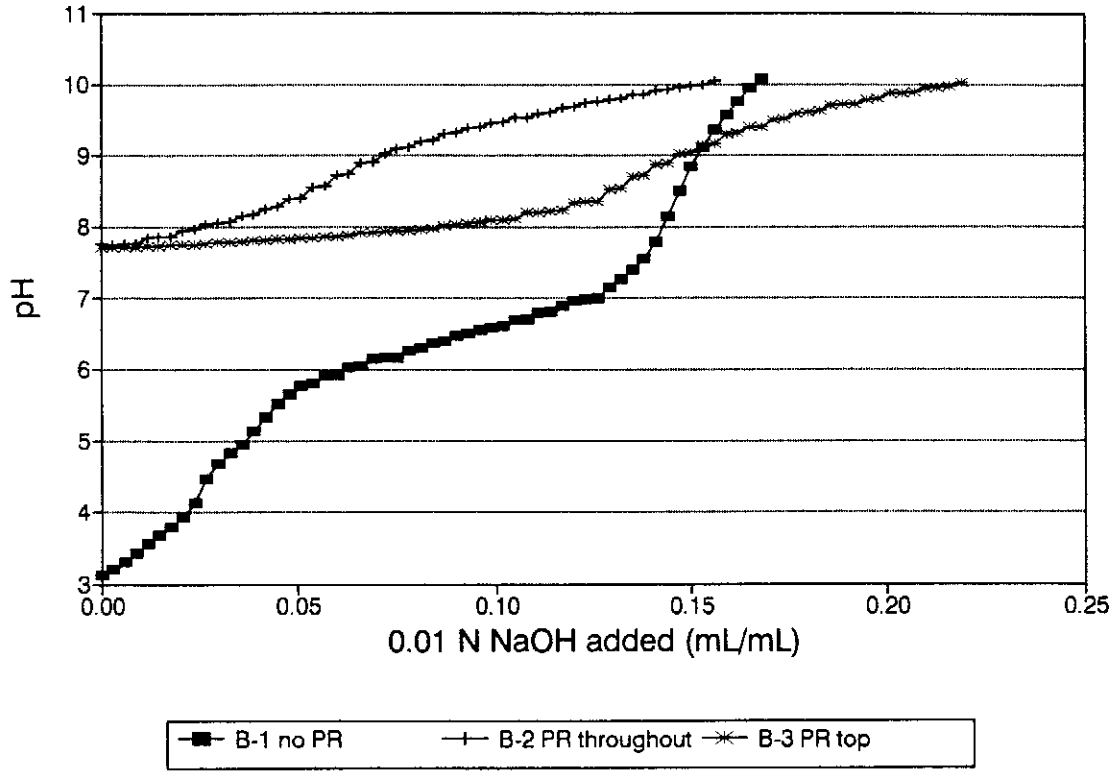
Waste Rock Drums
E,High Pyrite,Weathered-October 20,1993



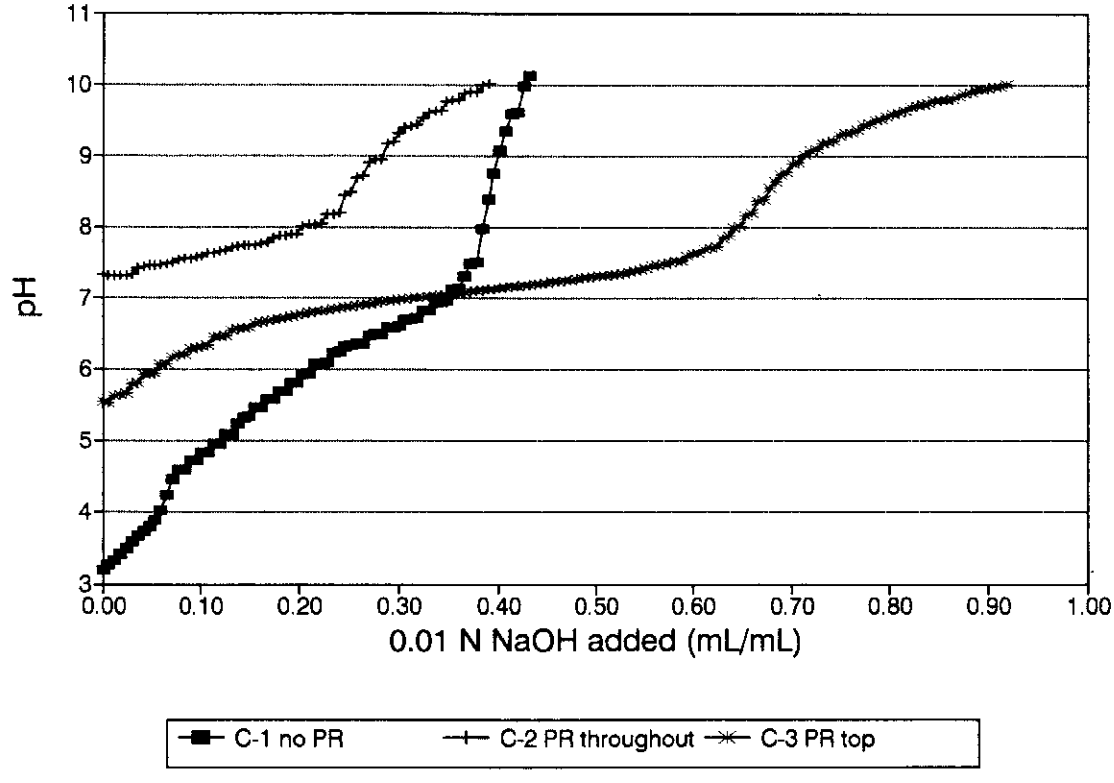
Waste Rock Drums
A,Low Pyrite, Fresh-February 19,1994



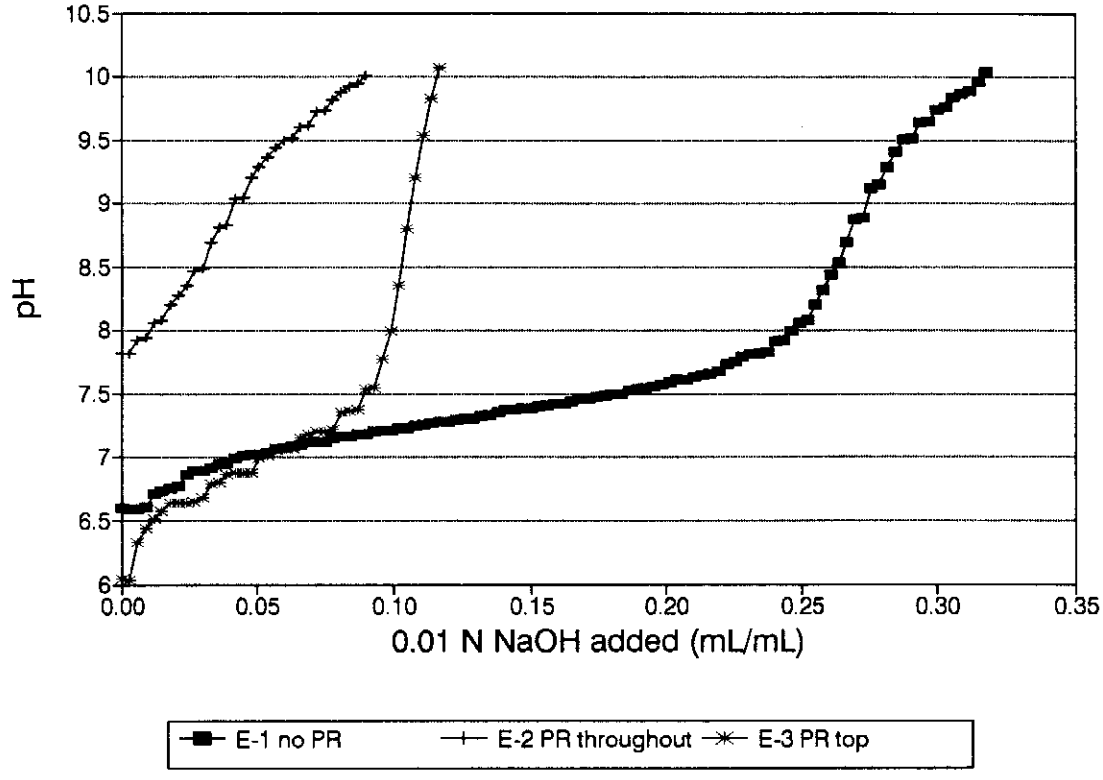
Waste Rock Drums
B,High Pyrite, Fresh-February 19,1994



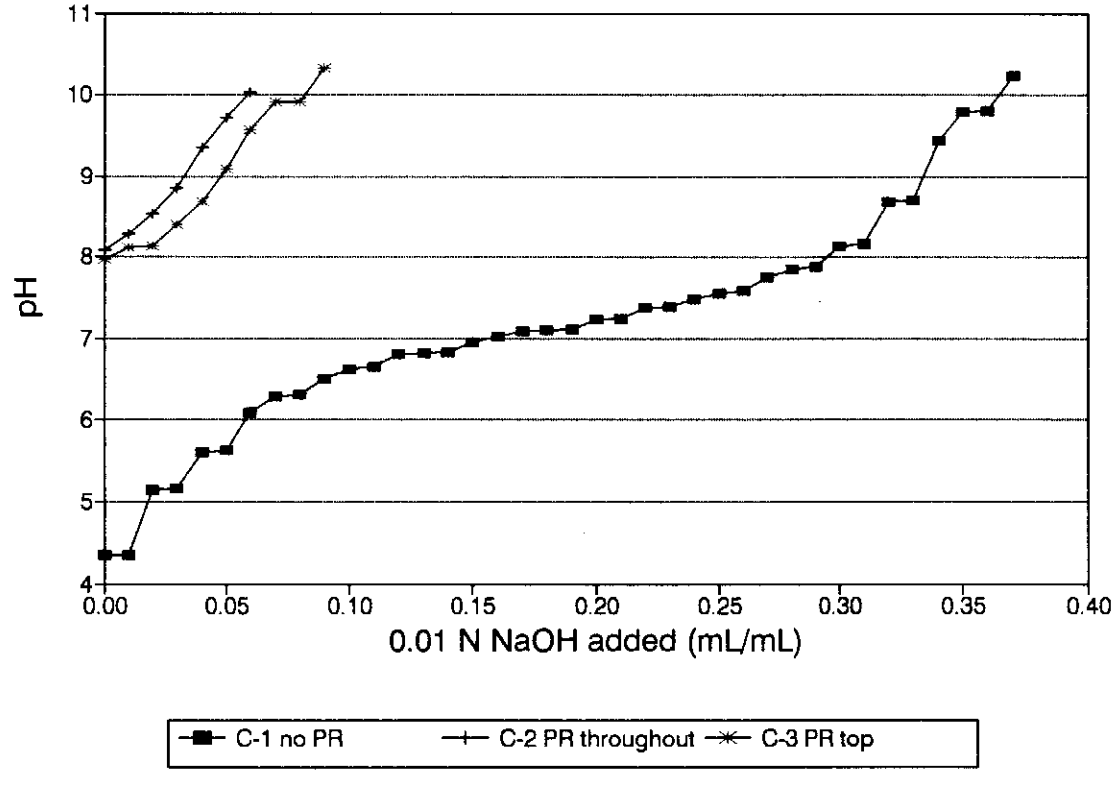
Waste Rock Drums
C,Low Pyrite,Weathered-February 19,1994



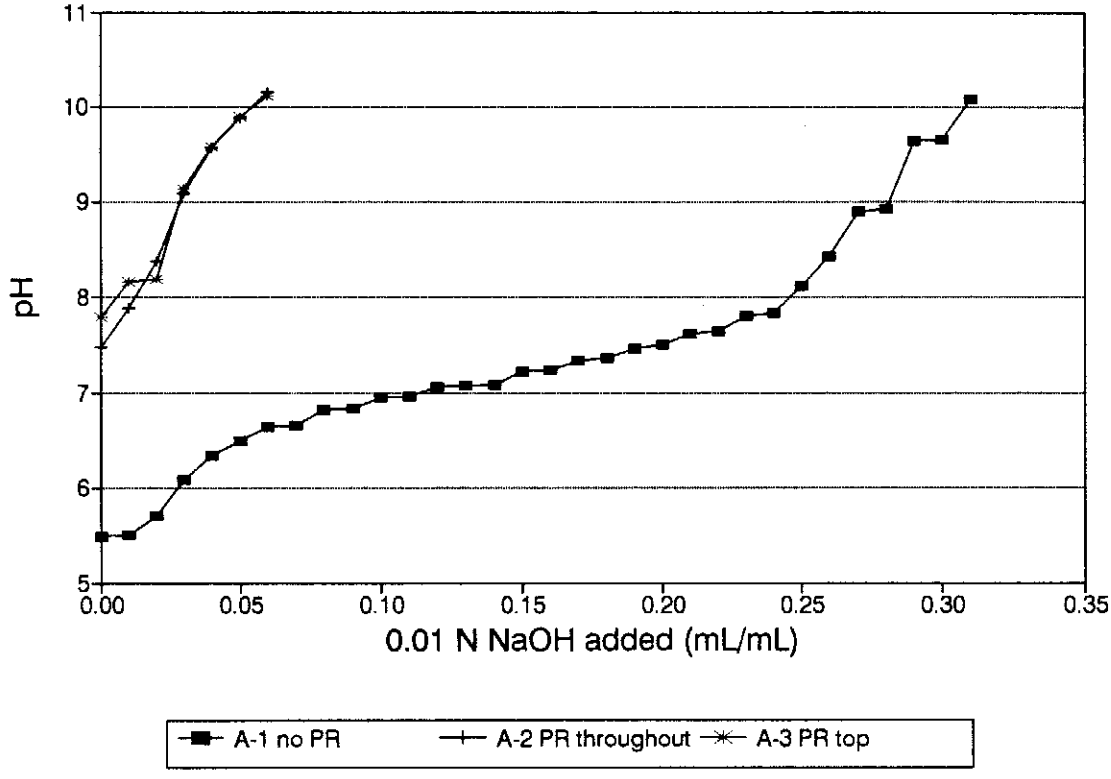
Waste Rock Drums
E,High Pyrite,Weathered-Feb 19,1994



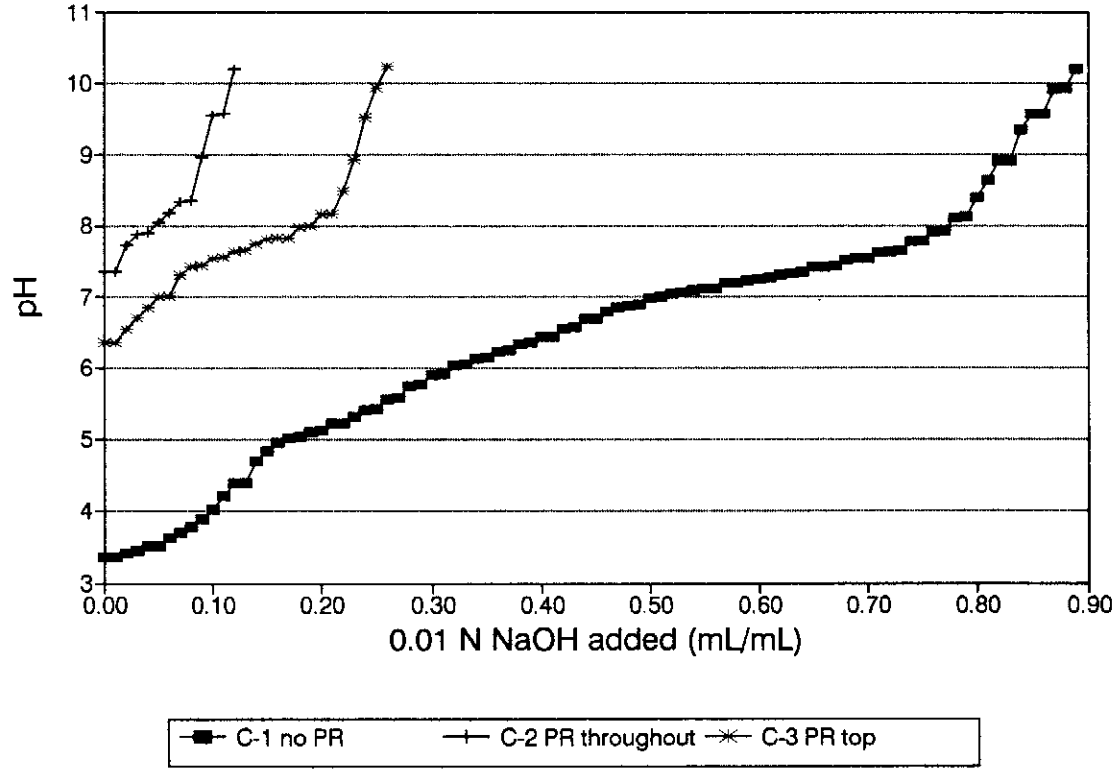
Waste Rock Drums
B,High Pyrite, Fresh-June 2,1994

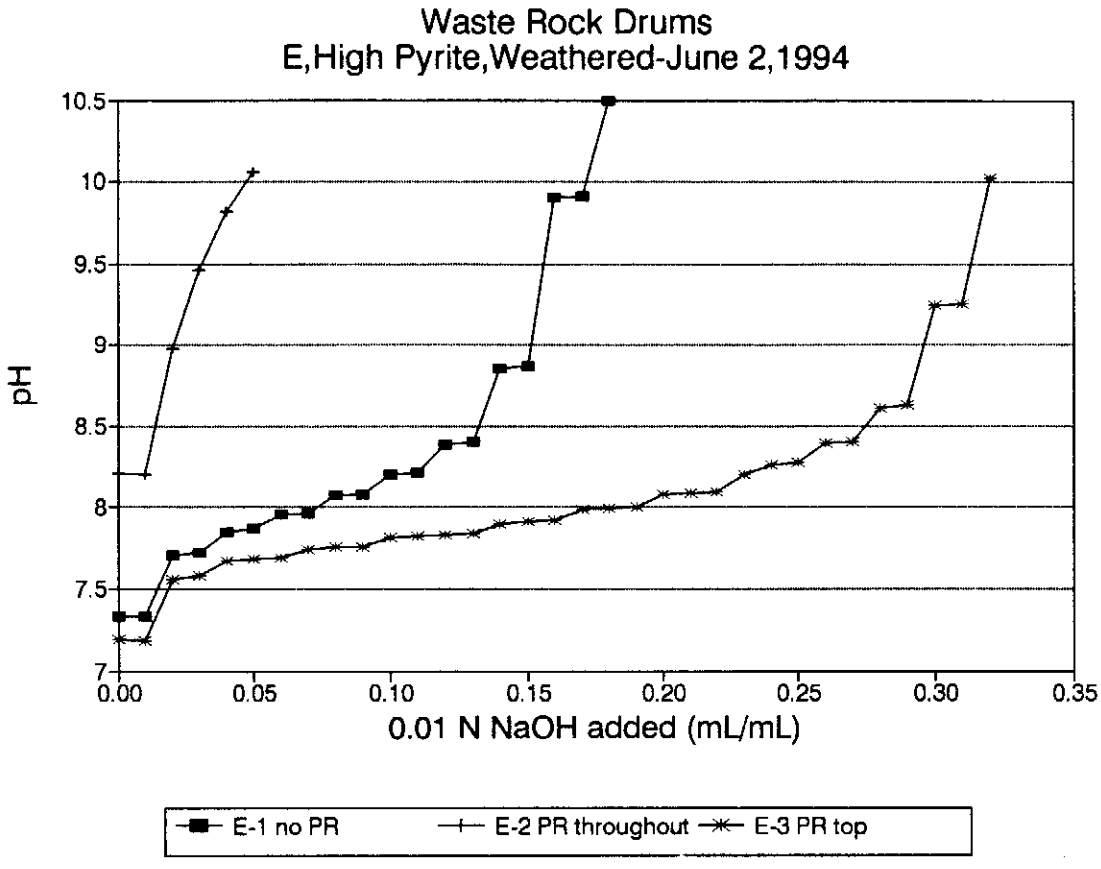


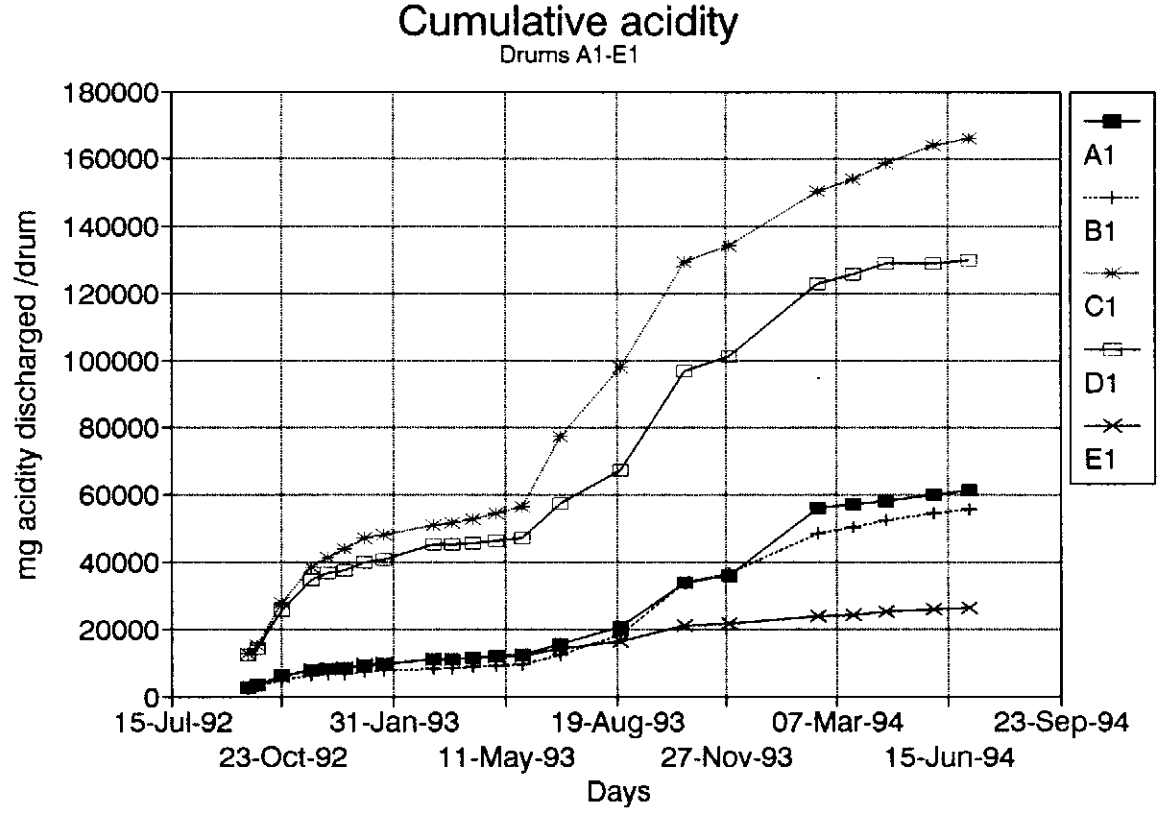
Waste Rock Drums
A,Low Pyrite, Fresh-June 2,1994

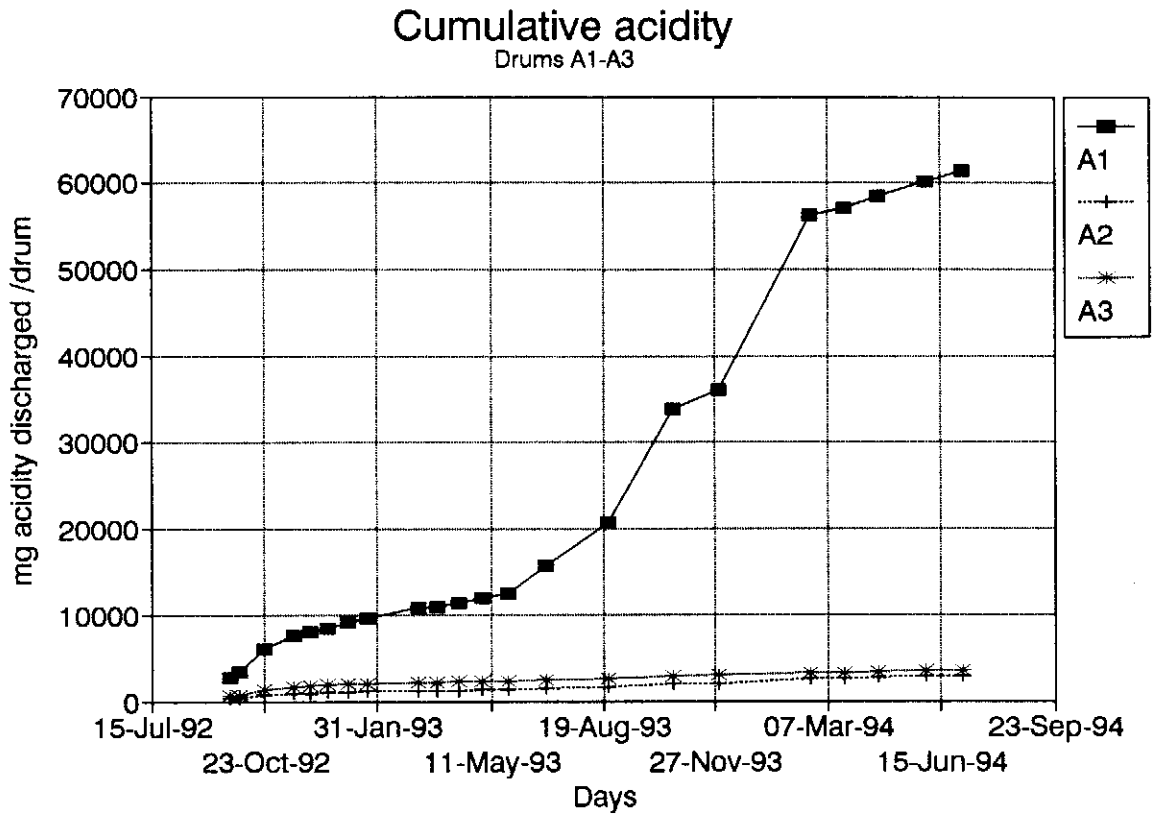


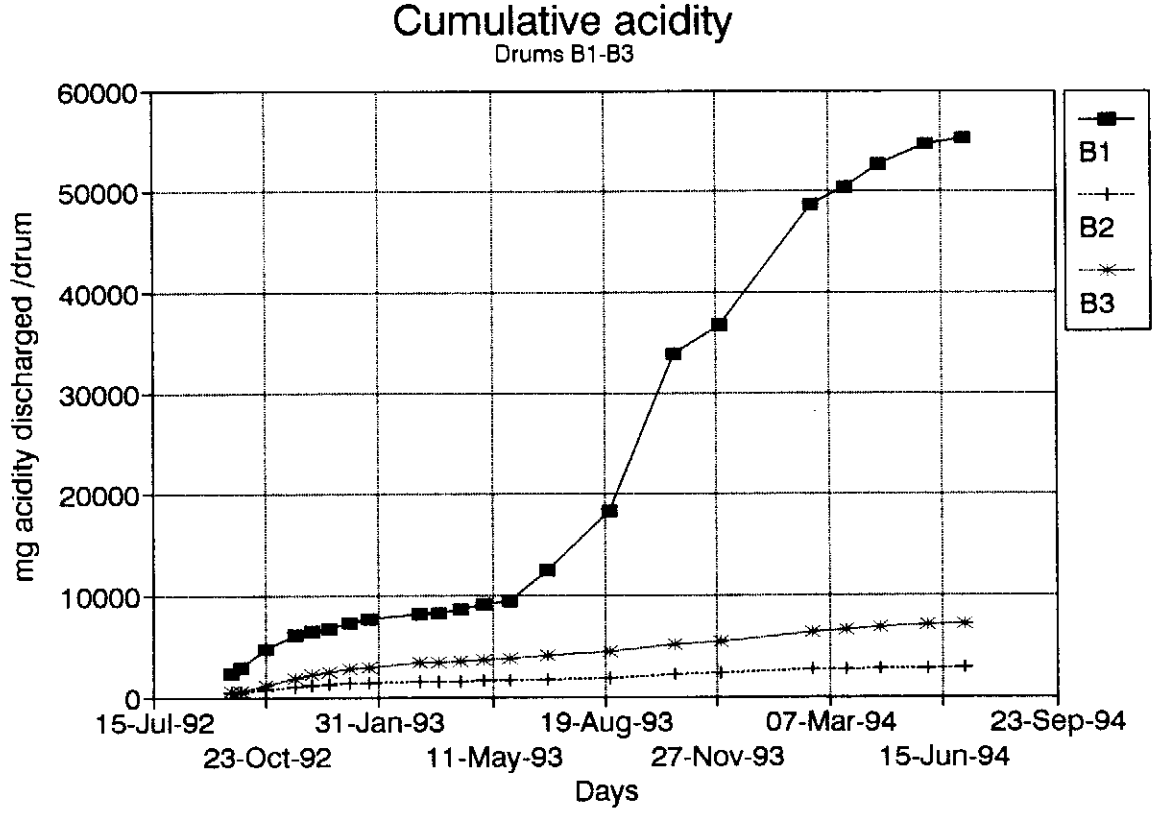
Waste Rock Drums
C,Low Pyrite,Weathered-June 2,1994

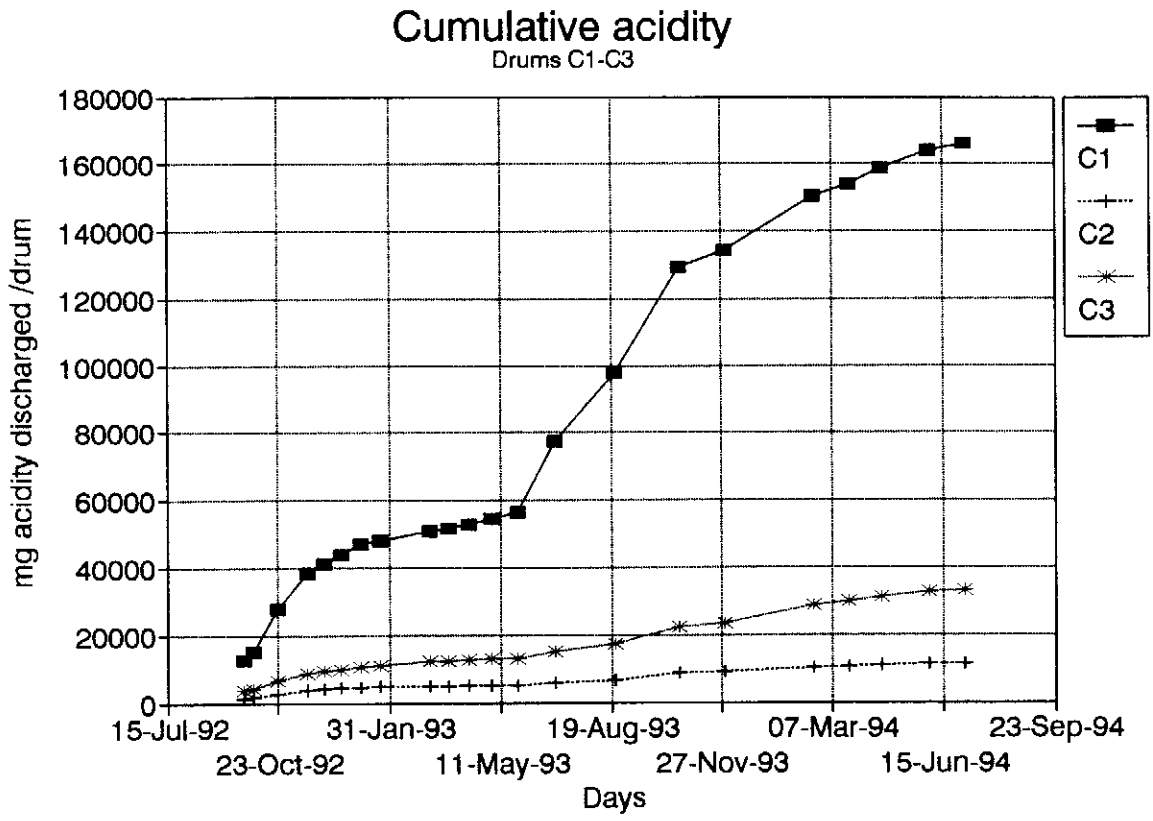


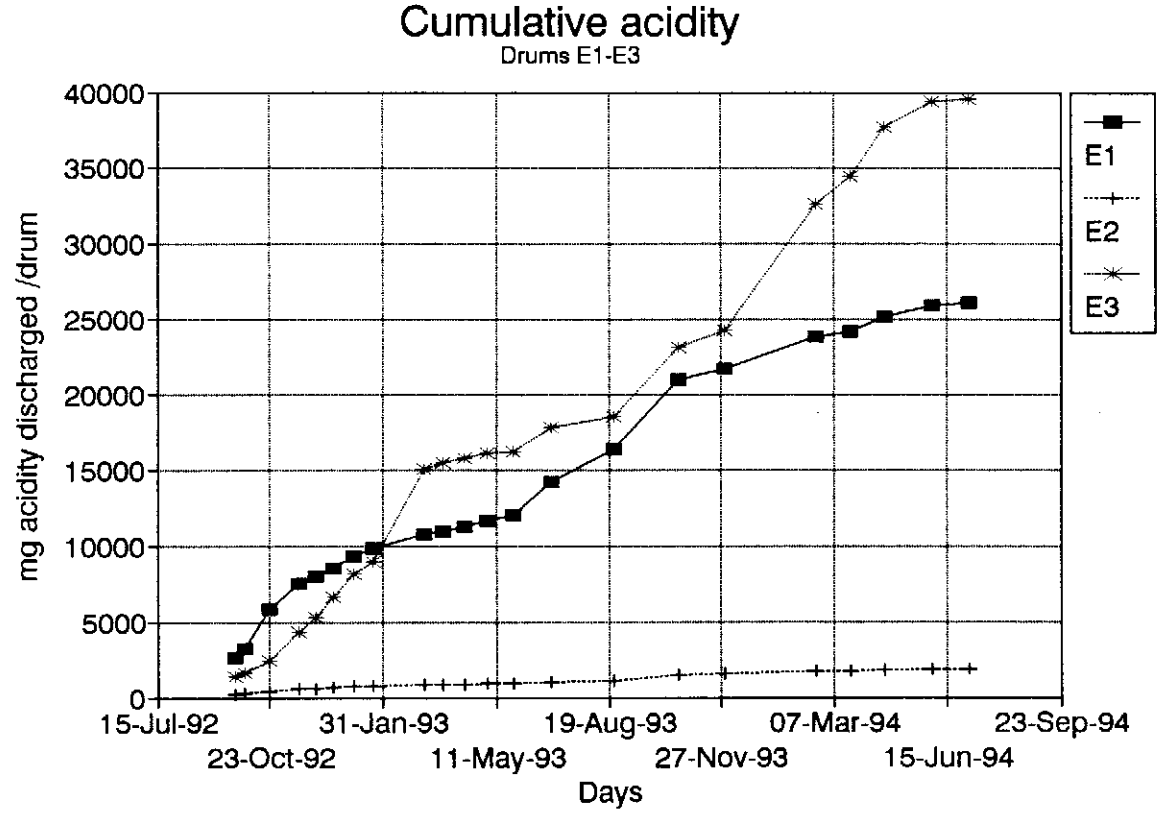

Waste Rock Drums
E,High Pyrite,Weathered-June 2,1994
pH
10.5
10
9.5
9
8.5
8
7.5
7
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.01 N NaOH added (mL/mL)
E-1 no PR
E-2 PR throughout
E-3 PR top

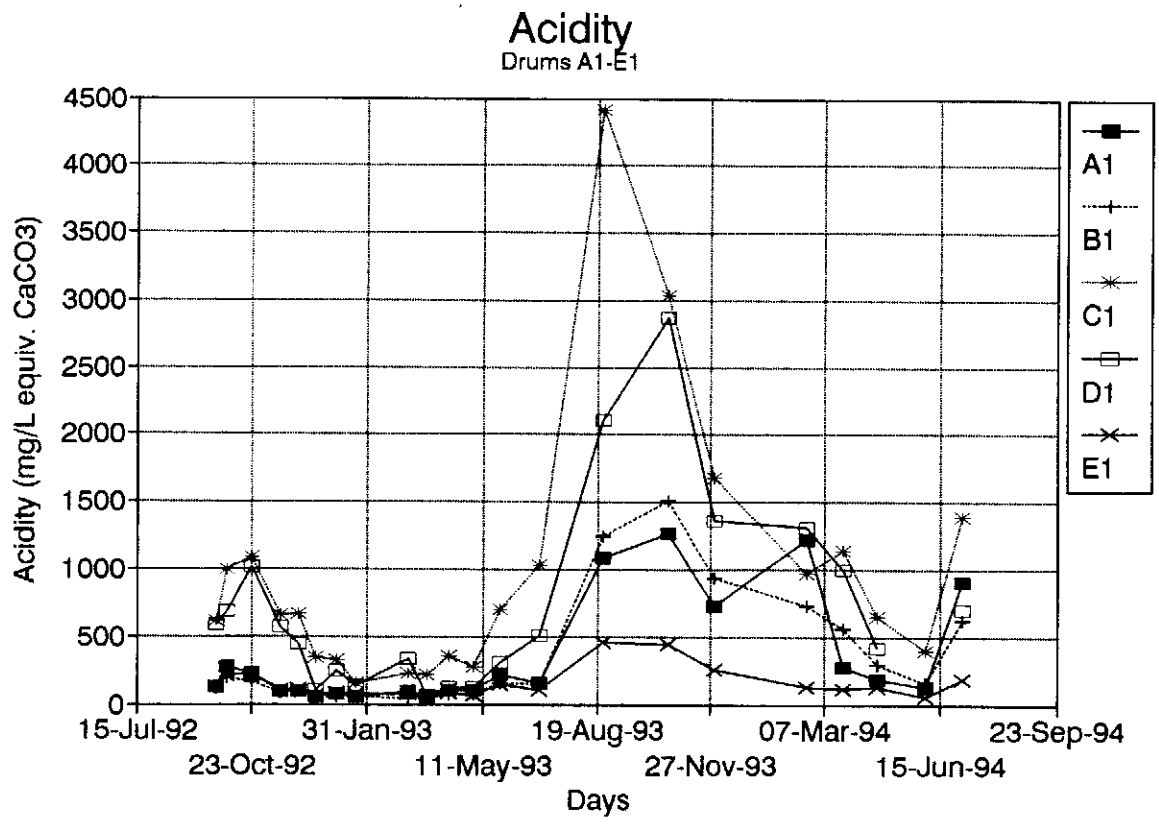

Cumulative acidity
Drums A1-E1
mg acidity discharged /drum
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
15-Jul-92
23-Oct-92
31-Jan-93
11-May-93
19-Aug-93
27-Nov-93
07-Mar-94
15-Jun-94
23-Sep-94
Days
A1
B1
C1
D1
E1

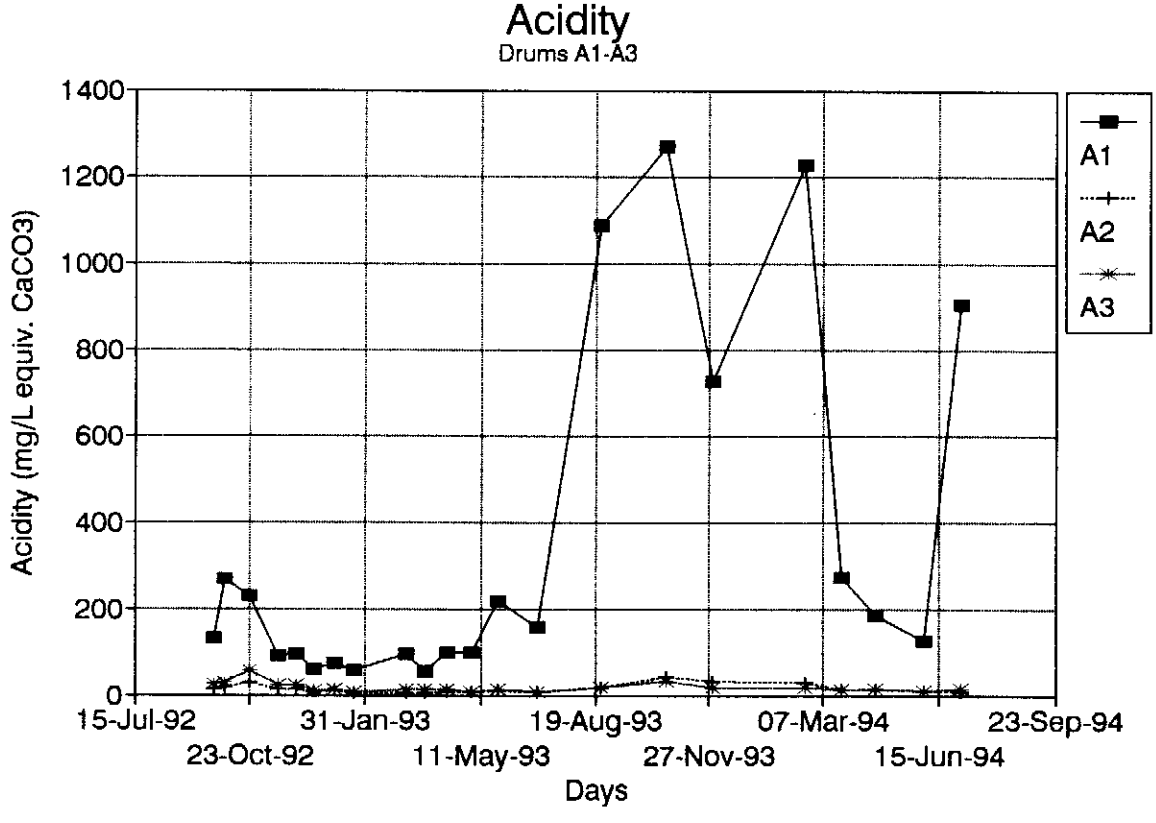

Cumulative acidity
Drums A1-A3
mg acidity discharged /drum
70000
60000
50000
40000
30000
20000
10000
0
15-Jul-92
23-Oct-92
31-Jan-93
11-May-93
19-Aug-93
27-Nov-93
07-Mar-94
15-Jun-94
23-Sep-94
Days
A1
A2
A3


Cumulative acidity
Drums B1-B3
mg acidity discharged /drum
60000
50000
40000
30000
20000
10000
0
15-Jul-92
23-Oct-92
31-Jan-93
11-May-93
19-Aug-93
27-Nov-93
07-Mar-94
15-Jun-94
23-Sep-94
Days
B1
B2
B3


Cumulative acidity
Drums C1-C3
mg acidity discharged /drum
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
15-Jul-92
23-Oct-92
31-Jan-93
11-May-93
19-Aug-93
27-Nov-93
07-Mar-94
15-Jun-94
23-Sep-94
Days
C1
C2
C3


Cumulative acidity
Drums E1-E3
mg acidity discharged /drum
40000
35000
30000
25000
20000
15000
10000
5000
0
15-Jul-92
23-Oct-92
31-Jan-93
11-May-93
19-Aug-93
27-Nov-93
07-Mar-94
15-Jun-94
23-Sep-94
Days
E1
E2
E3


Acidity
Drums A1-E1
Acidity (mg/L equiv. CaCO3)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
A1
B1
C1
D1
E1
15-Jul-92
23-Oct-92
31-Jan-93
11-May-93
19-Aug-93
27-Nov-93
07-Mar-94
15-Jun-94
23-Sep-94
Days


Acidity
Drums A1-A3
Acidity (mg/L equiv. CaCO3)
1400
1200
1000
800
600
400
200
0
A1
A2
A3
15-Jul-92
23-Oct-92
31-Jan-93
11-May-93
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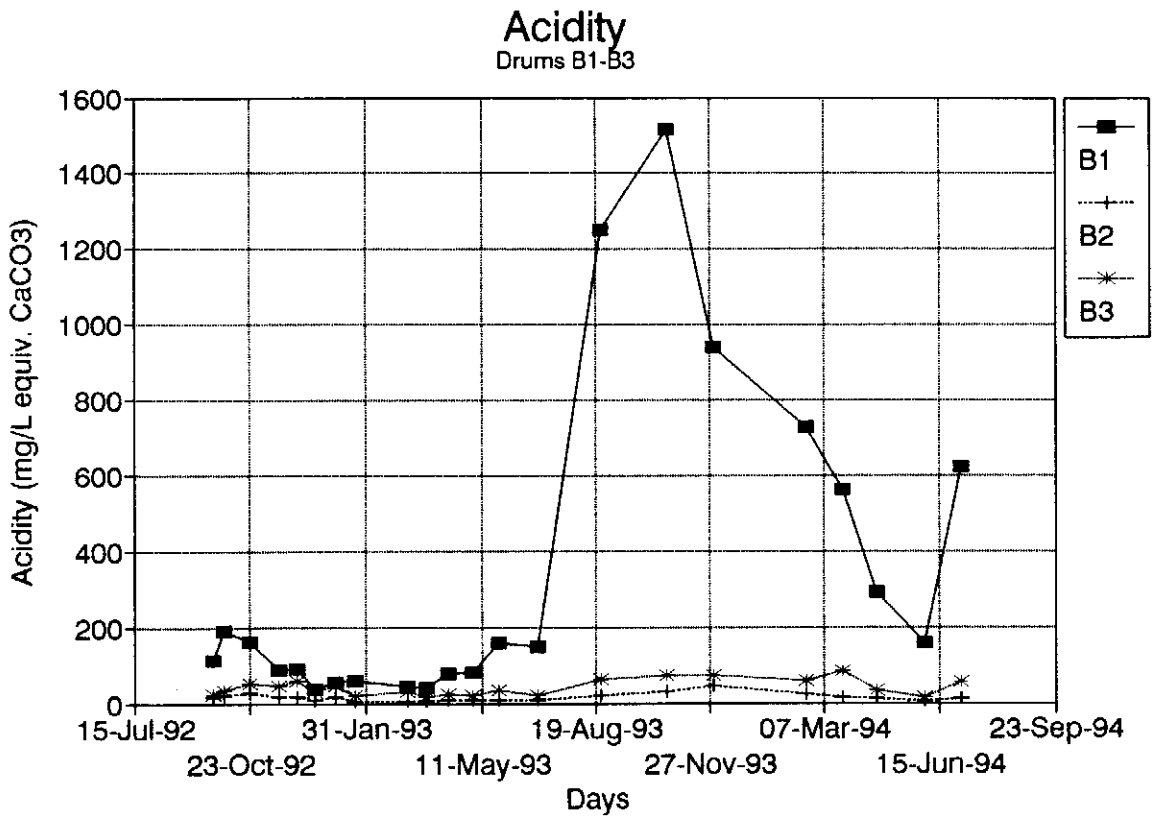
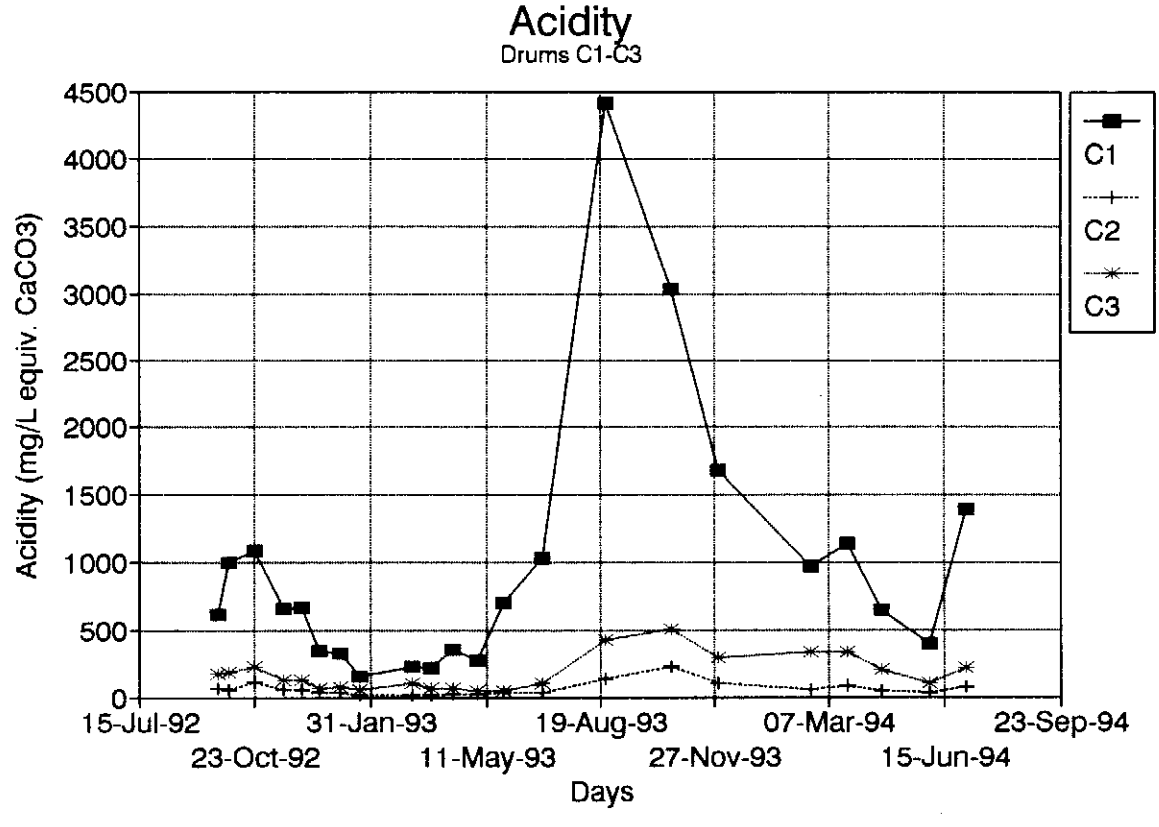
15-Jun-94
23-Sep-94
Days


Acidity
Drums B1-B3
Acidity (mg/L equiv. CaCO3)
1600
1400
1200
1000
800
600
400
200
0
B1
B2
B3
15-Jul-92
23-Oct-92
31-Jan-93
11-May-93
19-Aug-93
27-Nov-93
07-Mar-94
15-Jun-94
23-Sep-94
Days


Acidity
Drums C1-C3
Acidity (mg/L equiv. CaCO3)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
C1
C2
C3
15-Jul-92
23-Oct-92
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11-May-93
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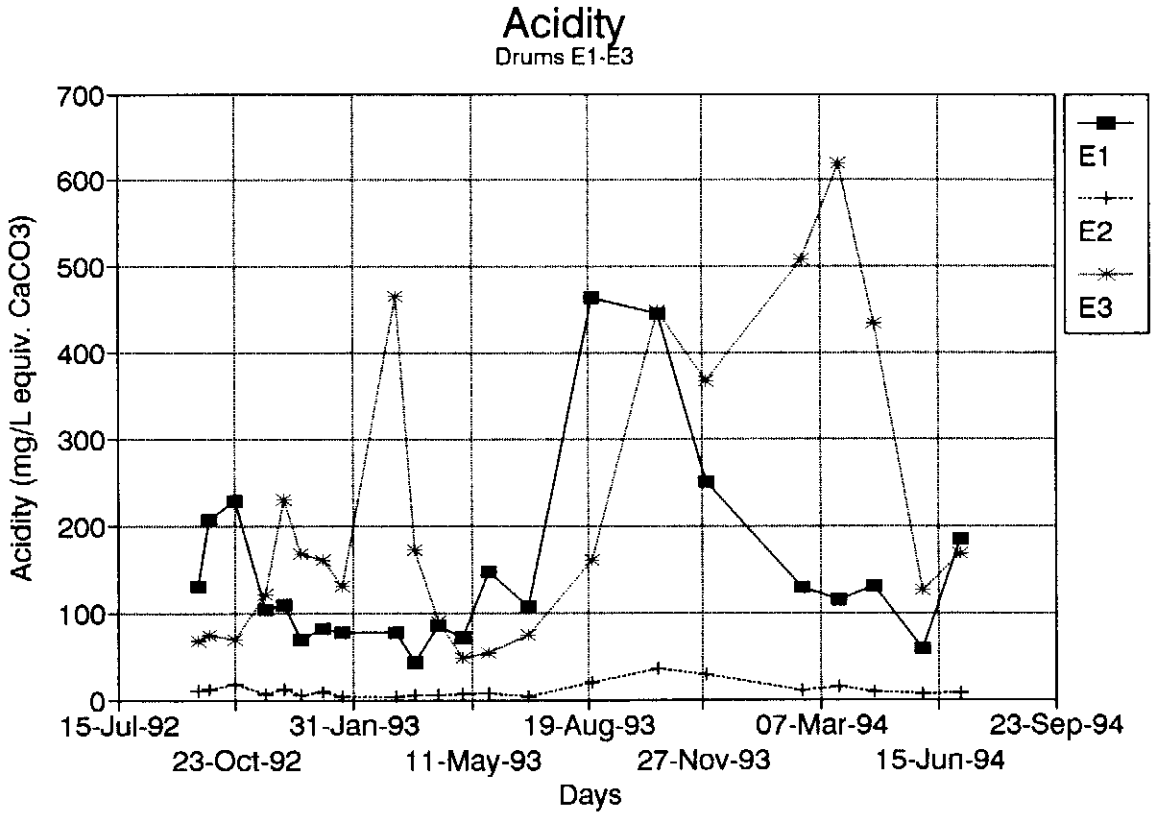
15-Jun-94
23-Sep-94
Days


Acidity
Drums E1-E3
Acidity (mg/L equiv. CaCO3)
700
600
500
400
300
200
100
0
E1
E2
E3
15-Jul-92
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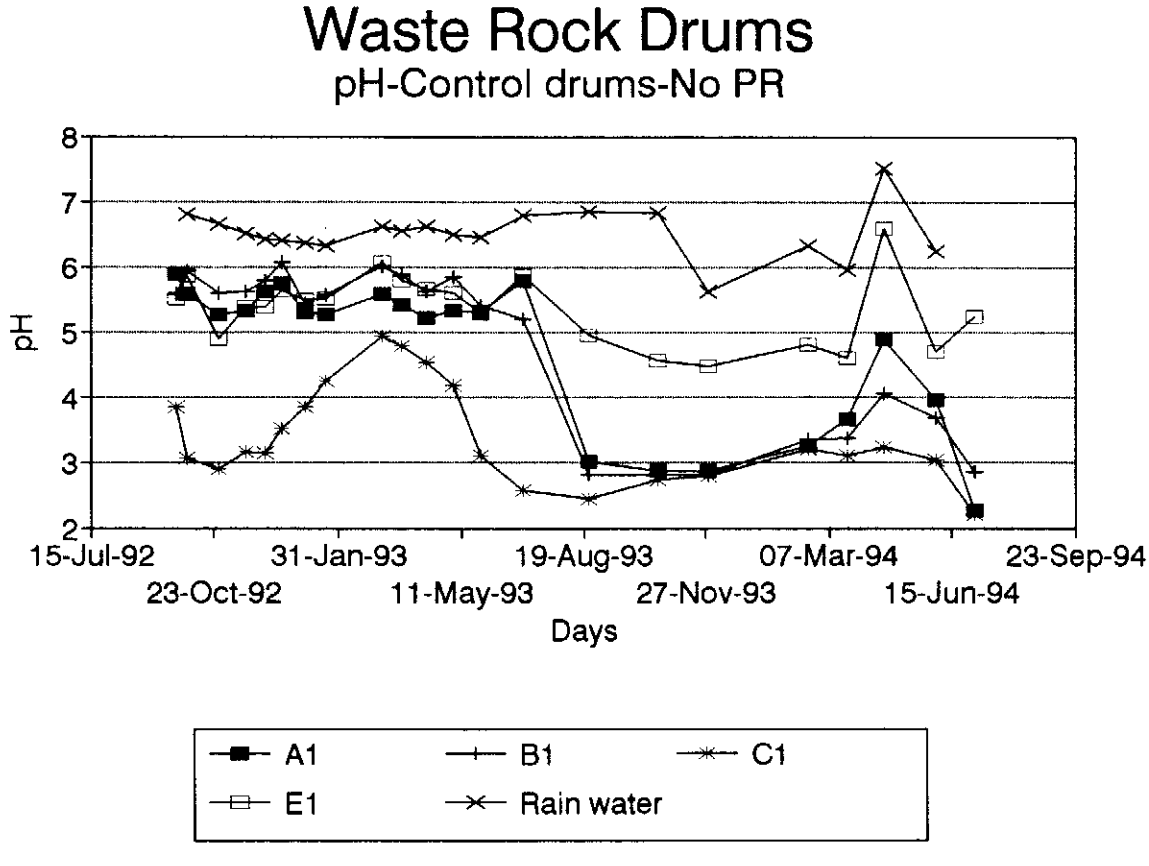
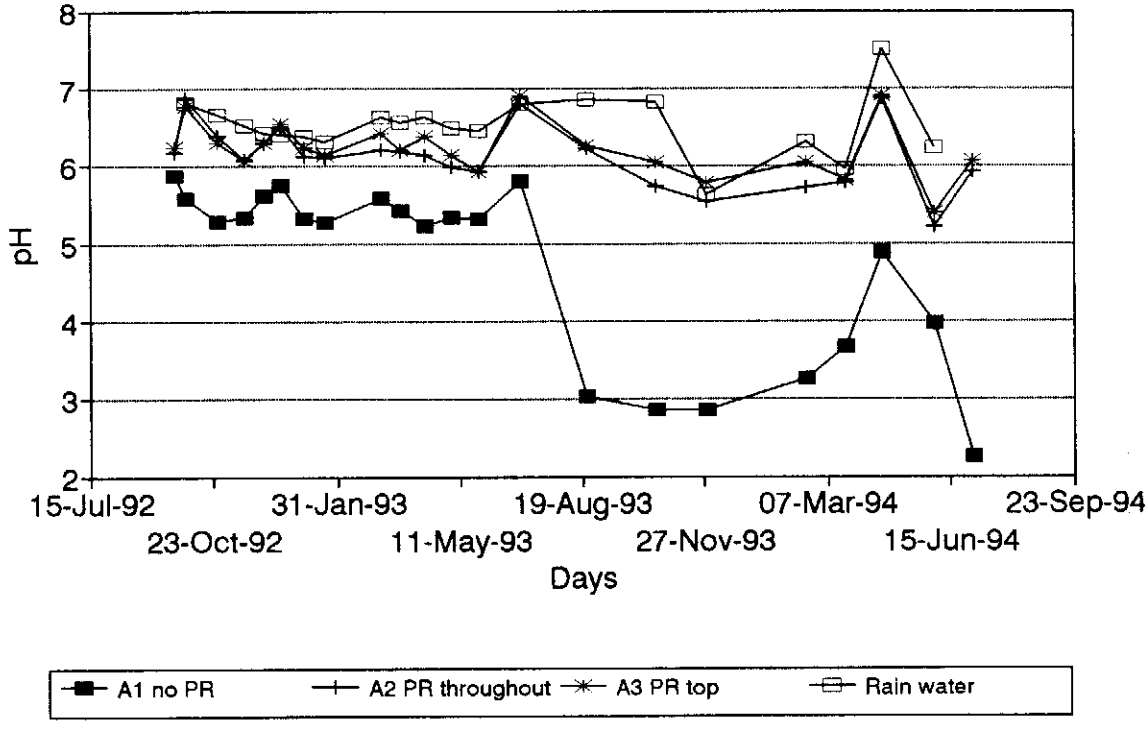
15-Jun-94
23-Sep-94
Days


Waste Rock Drums
pH-Control drums-No PR
pH
8
7
6
5
4
3
2
15-Jul-92
23-Oct-92
31-Jan-93
11-May-93
19-Aug-93
27-Nov-93
07-Mar-94
15-Jun-94
23-Sep-94
Days
A1
B1
C1
E1
Rain water

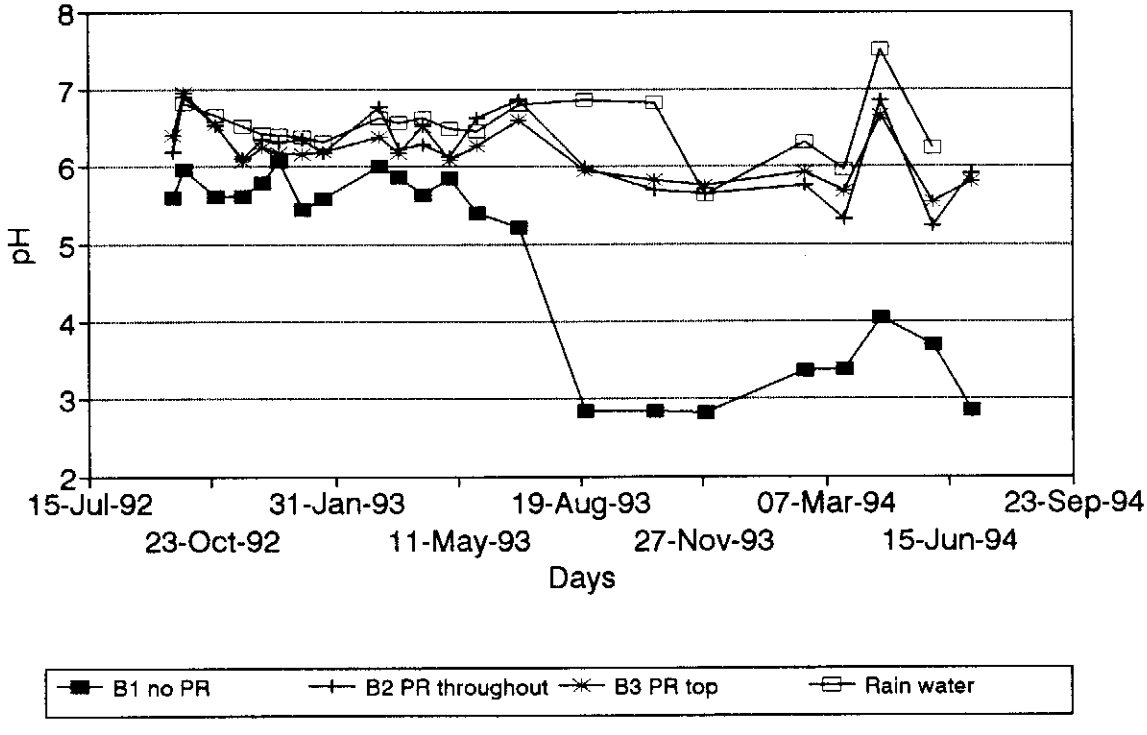
Waste Rock Drums

pH-A drums (low pyrite fresh)



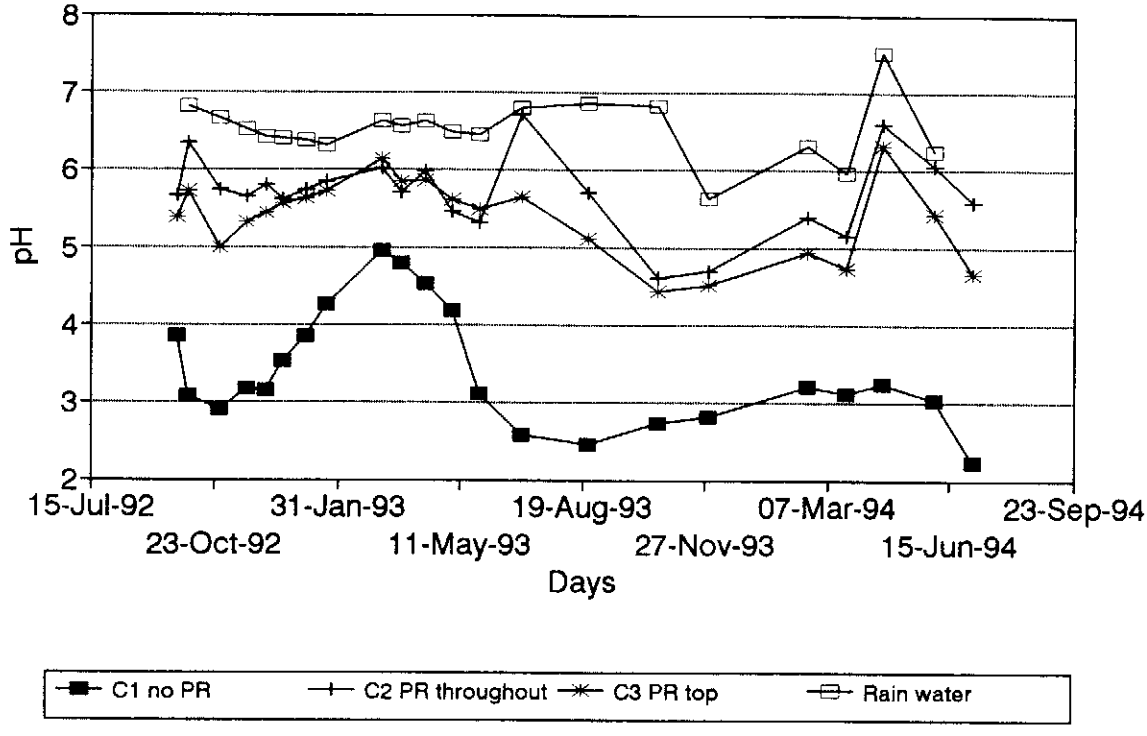
Waste Rock Drums

pH-B drums (high pyrite fresh)



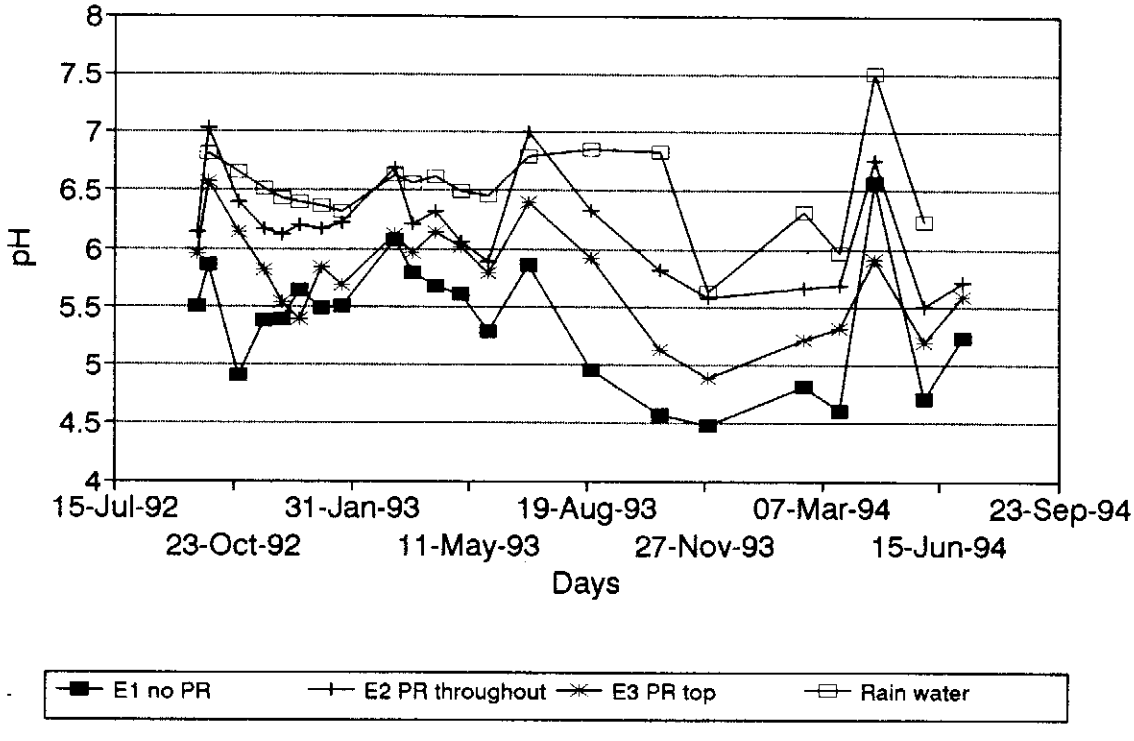
Waste Rock Drums

pH-C drums (low pyrite,wthd.>4y)



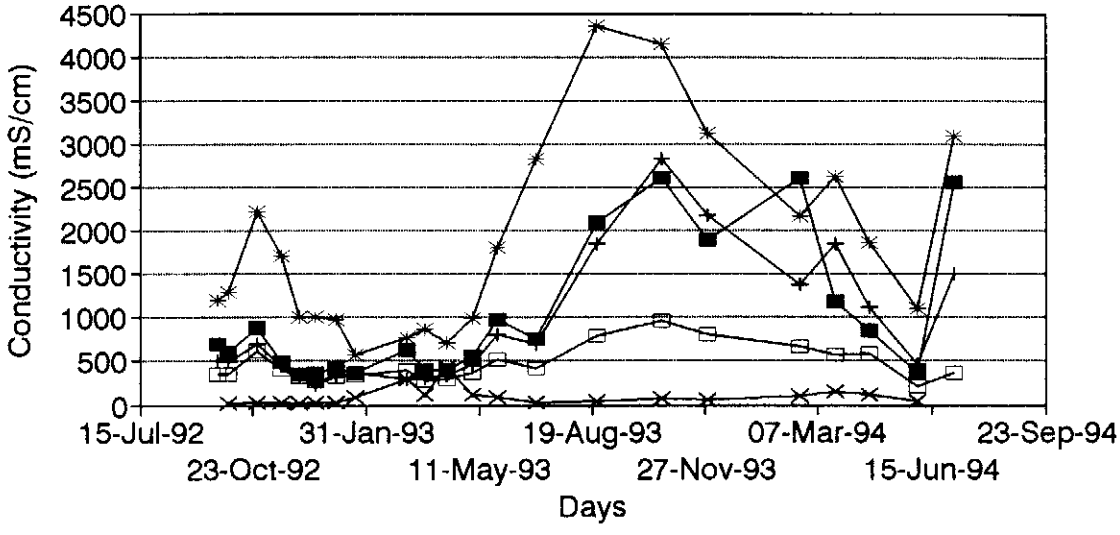
Waste Rock Drums

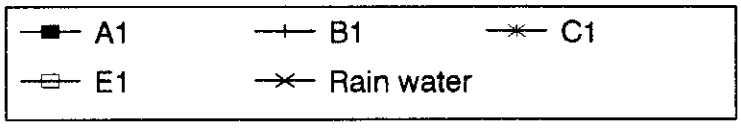
pH-E drums (high pyrite,wthrd.>4y)



Waste Rock Drums

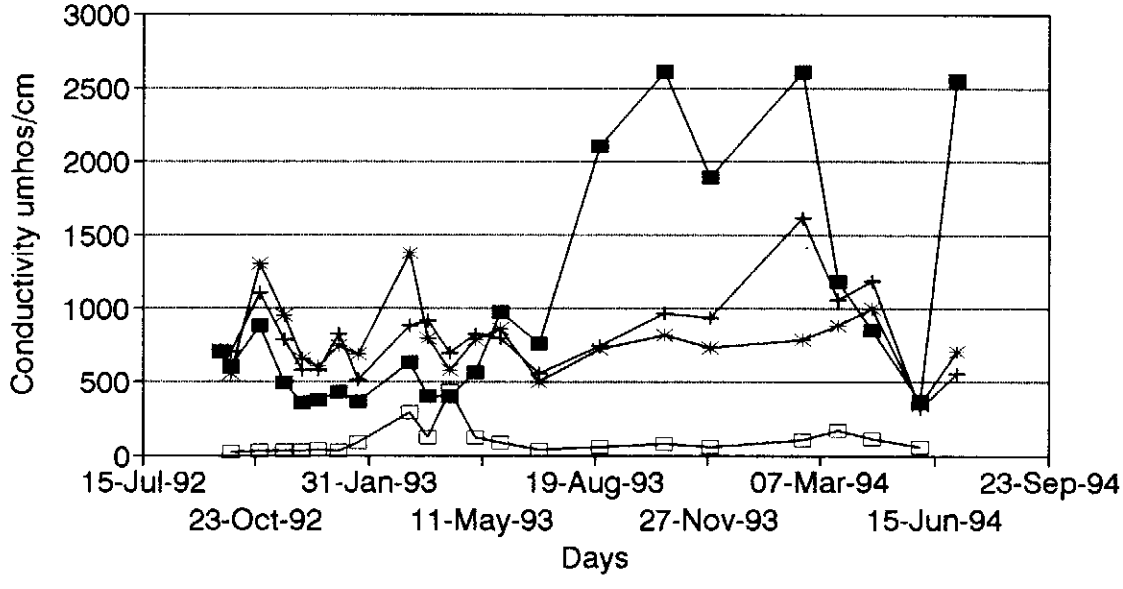
Conductivity-Control drums-No PR

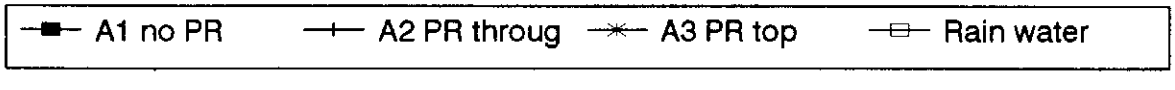




Waste Rock Drums

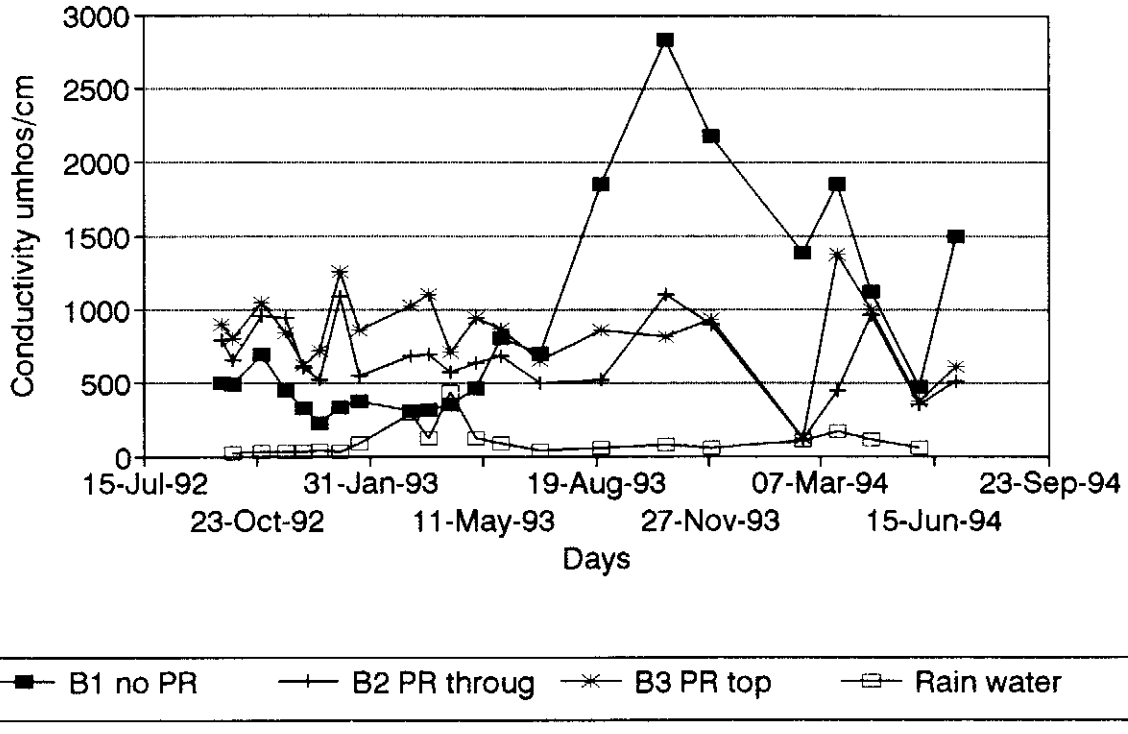
Conductivity-A drums (low pyrite fresh)





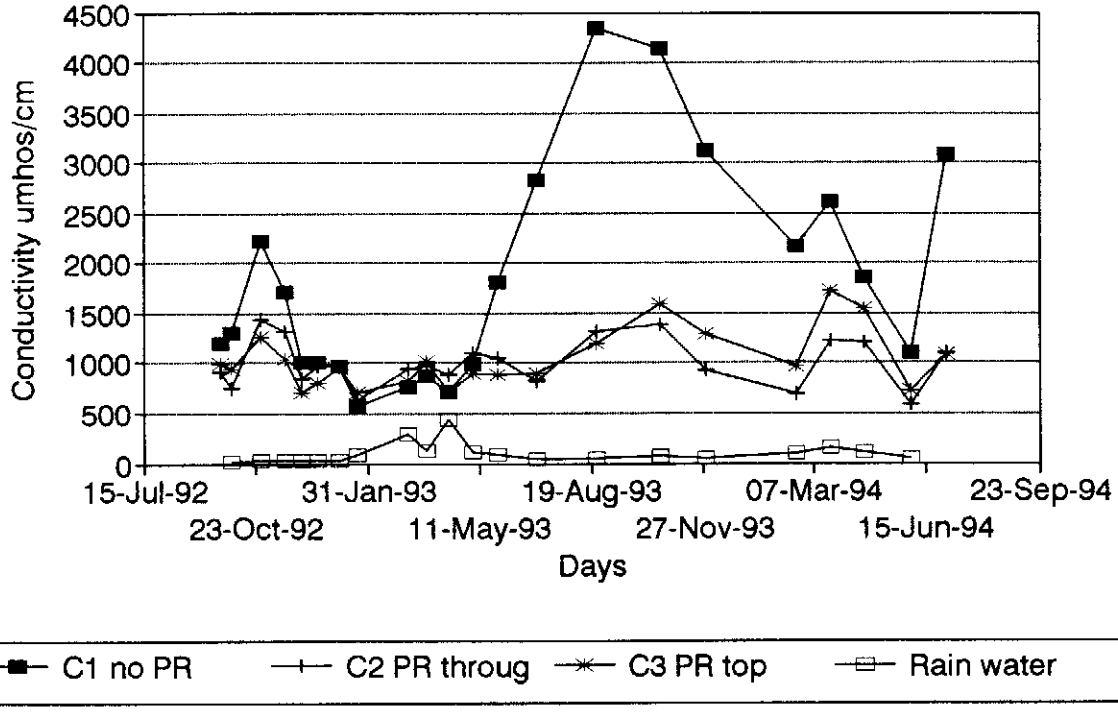
Waste Rock Drums

Conductivity-B drums(high pyrite fresh)



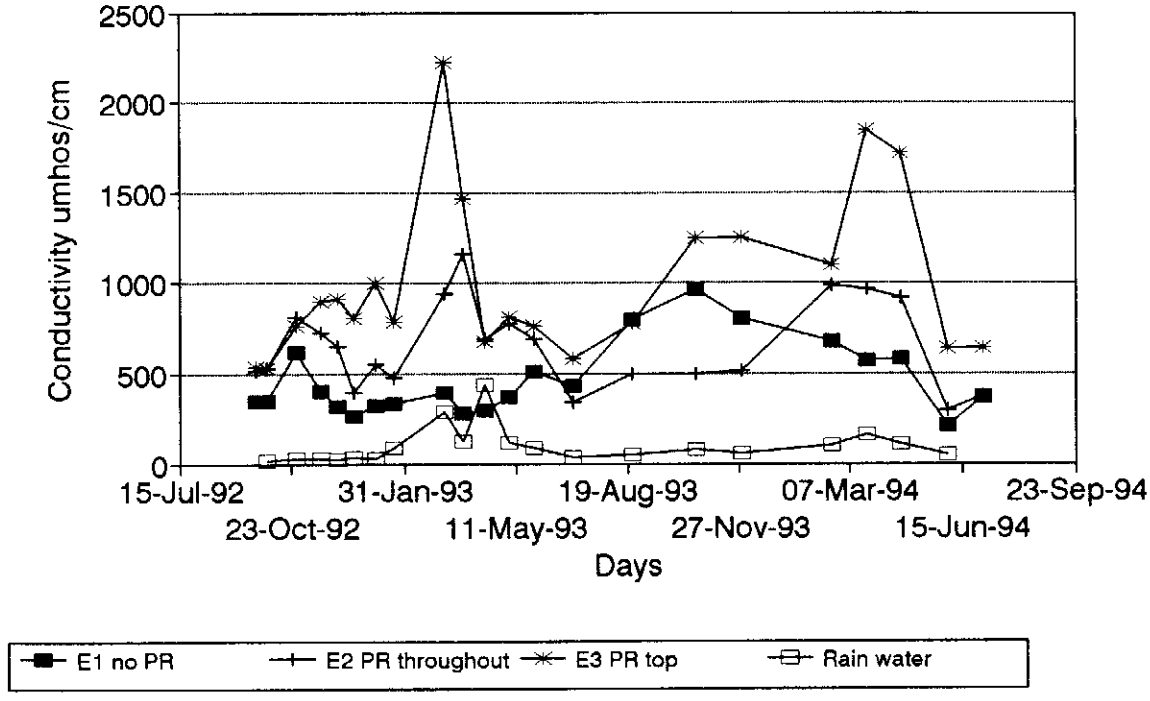
Waste Rock Drums

Conductivity-C drums(low pyrite, wthrd)



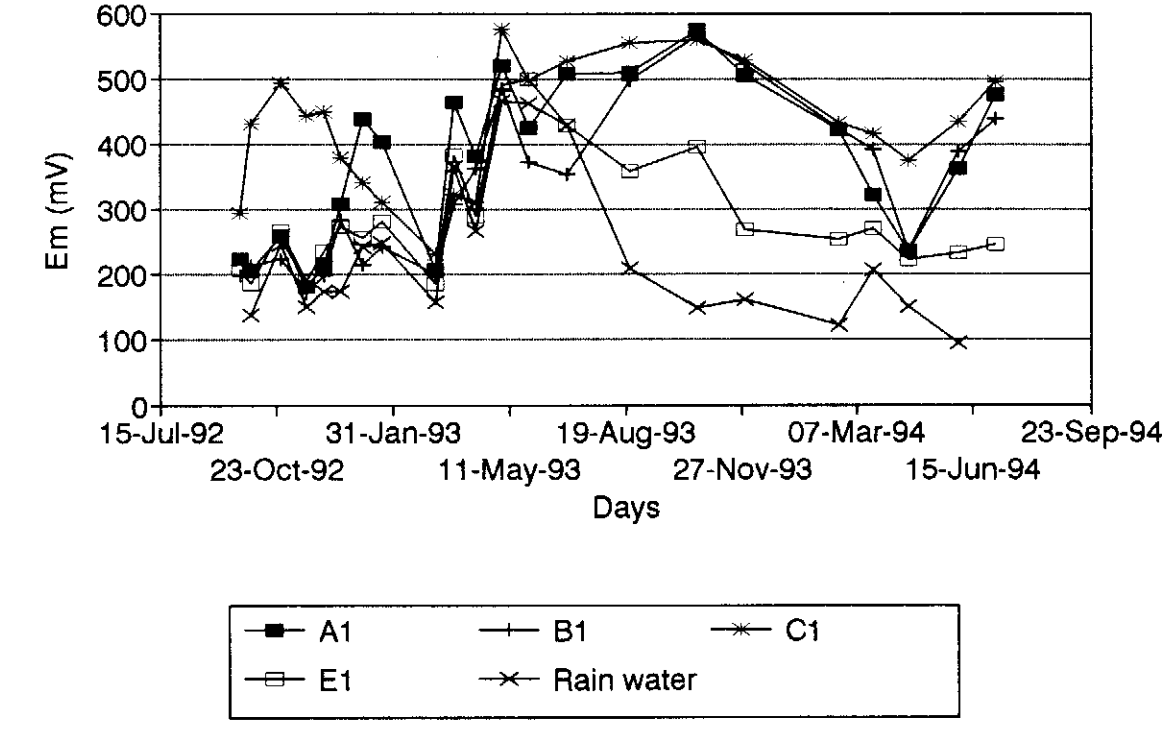
Waste Rock Drums

Conductivity-E drums(high pyr,wthd>4y)



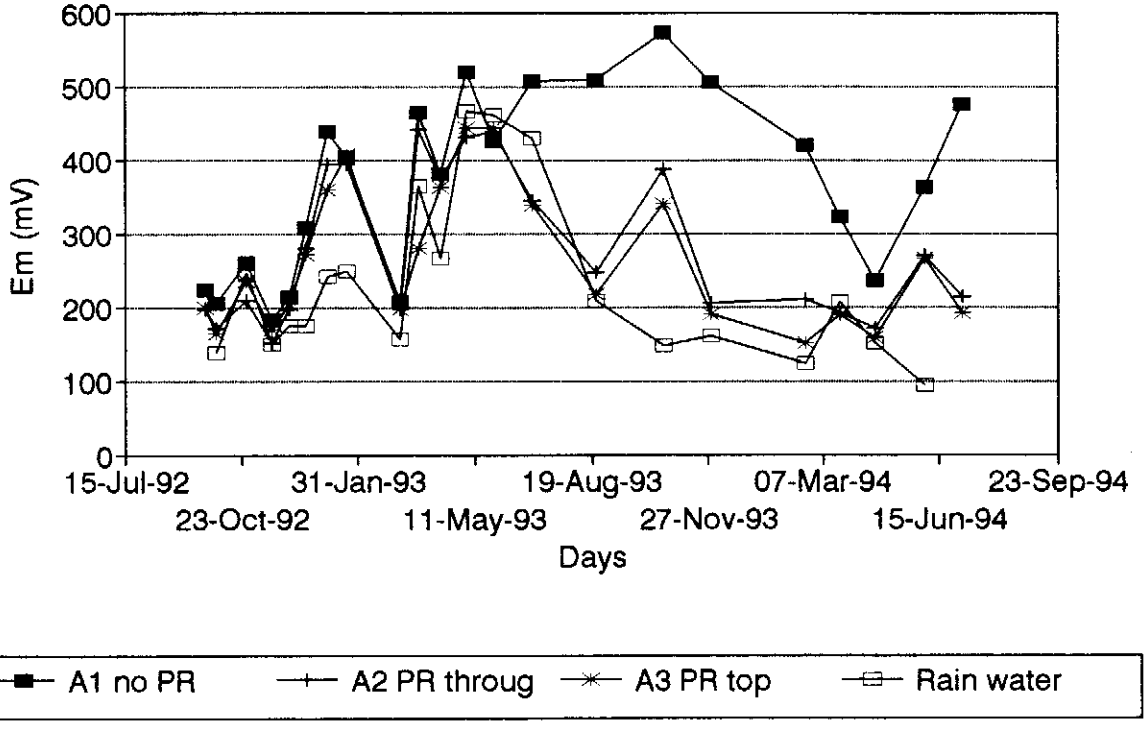
Waste Rock Drums

Em-Control drums-No PR



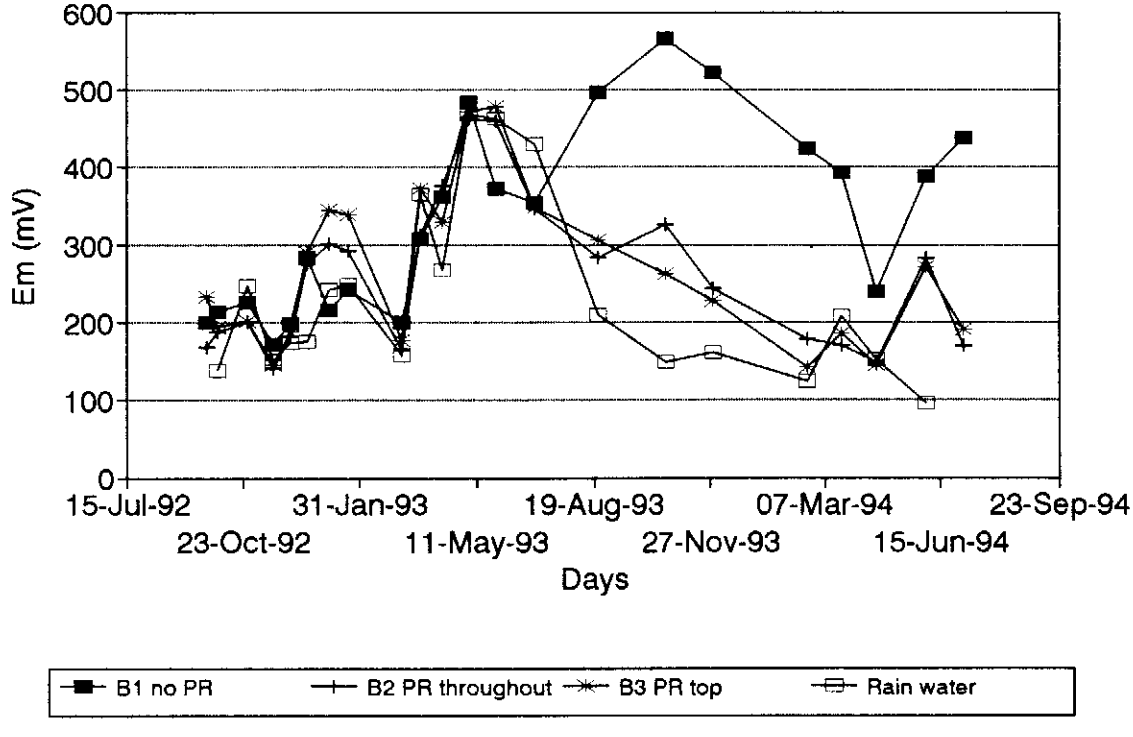
Waste Rock Drums

Em-A Drums (low pyrite, fresh)



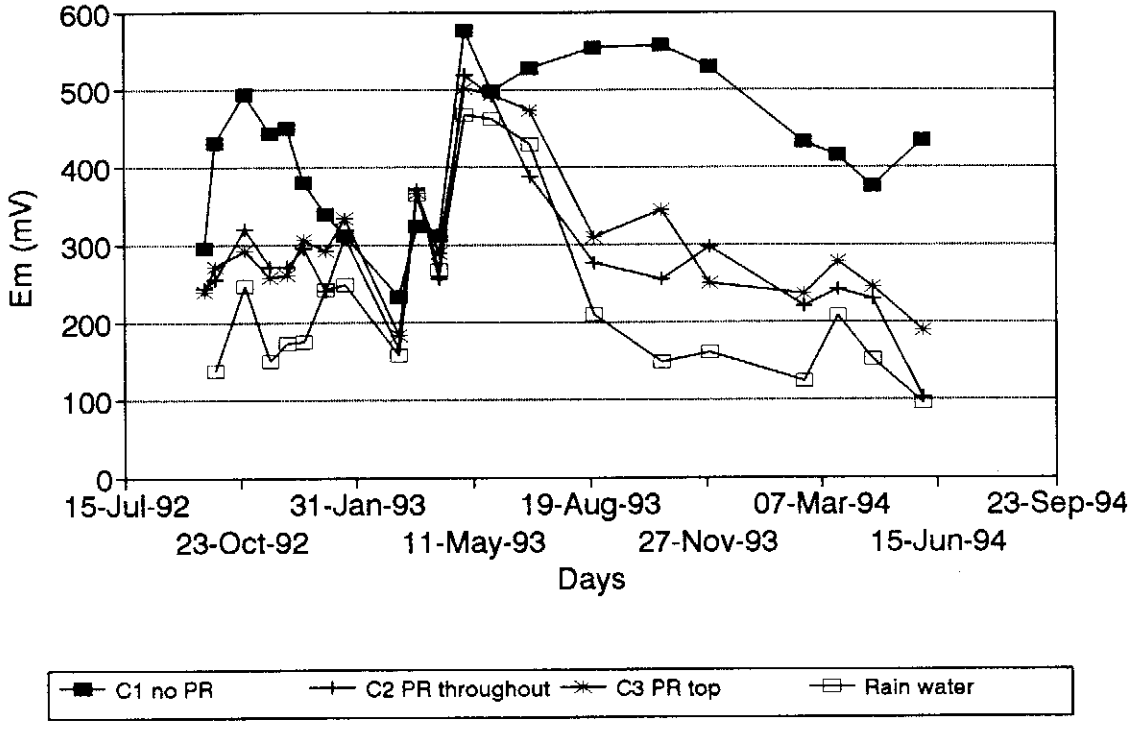
Waste Rock Drums

Em-B drums (high pyrite, fresh)



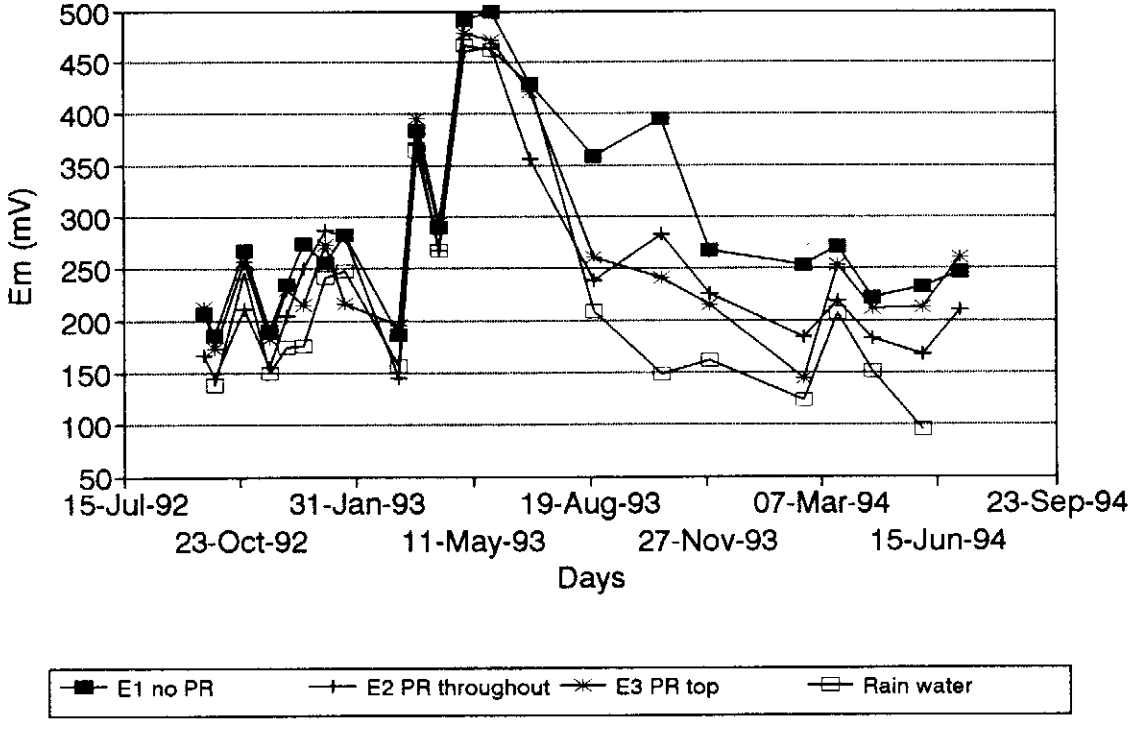
Waste Rock Drums

Em-C drums (low pyrite,wthd.>4y)



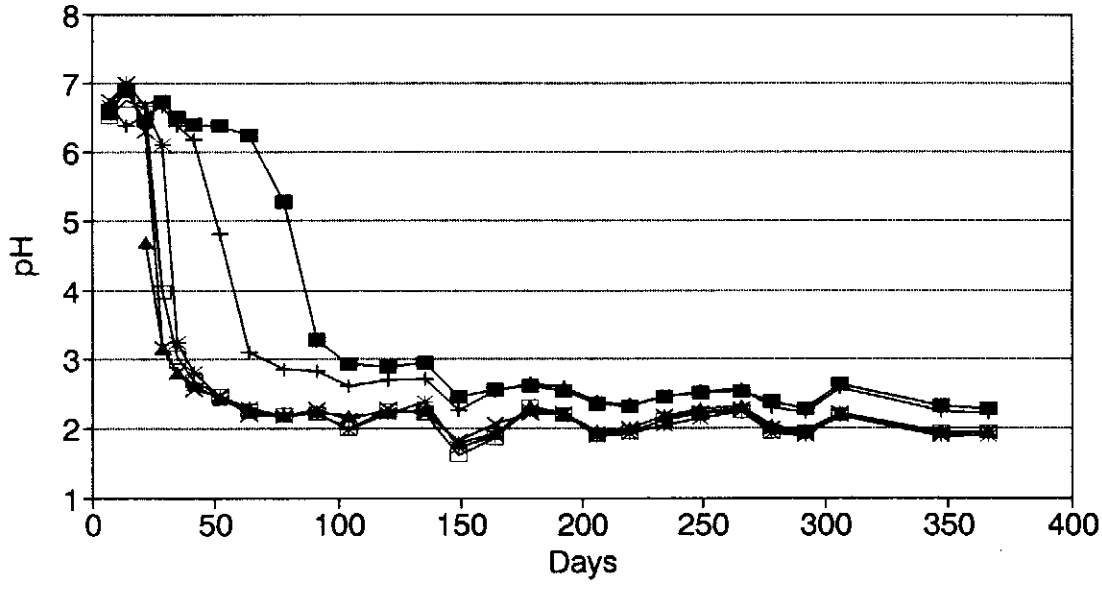
Waste Rock Drums

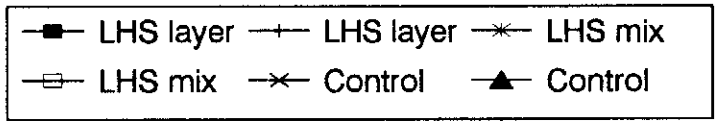
Em-E drums(high pyr.,wthd.>4y)



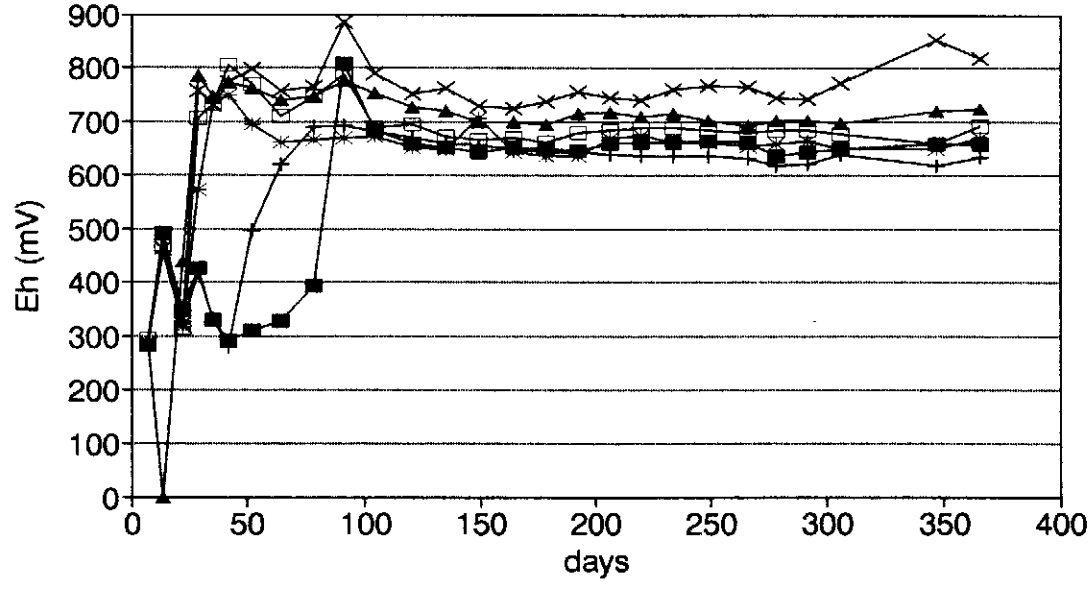
COAL WASTE COLUMNS

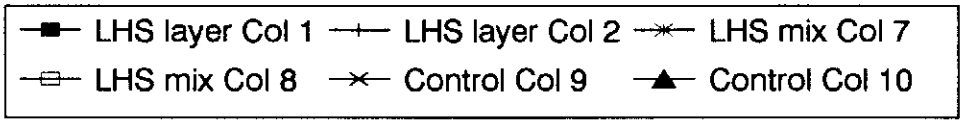
PERD Columns
Long Harbour Sand - pH

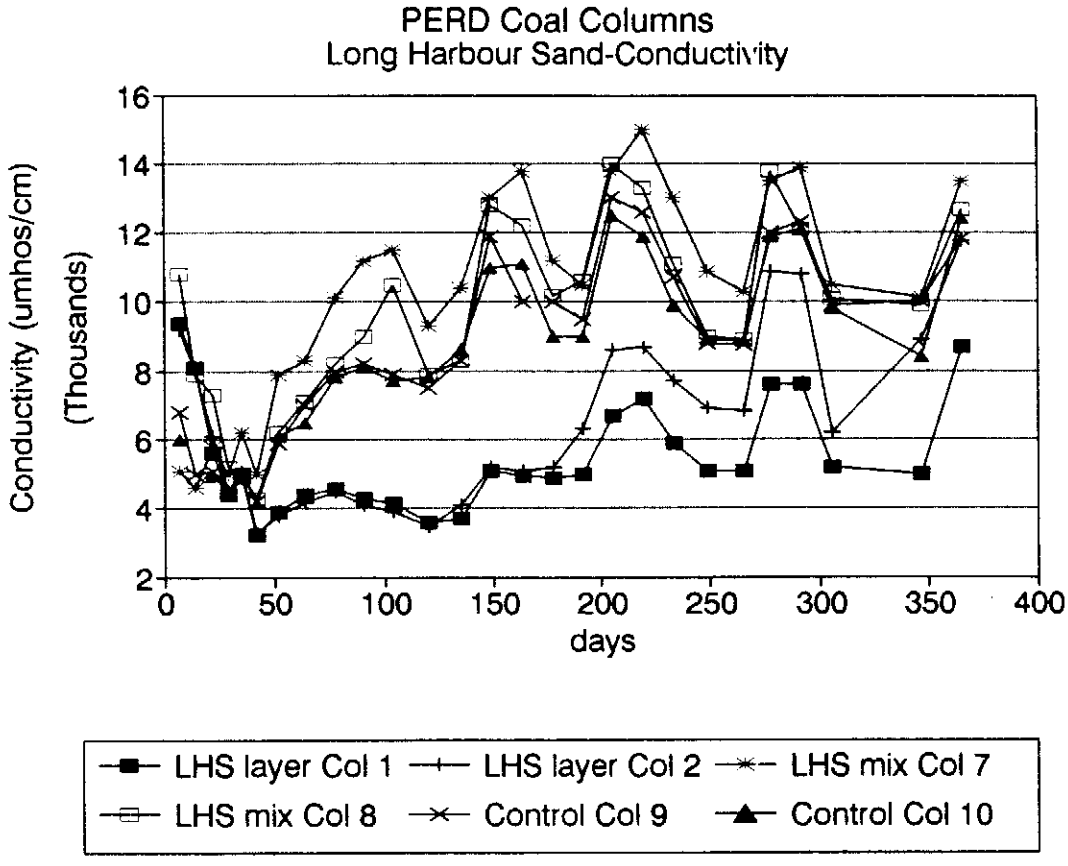


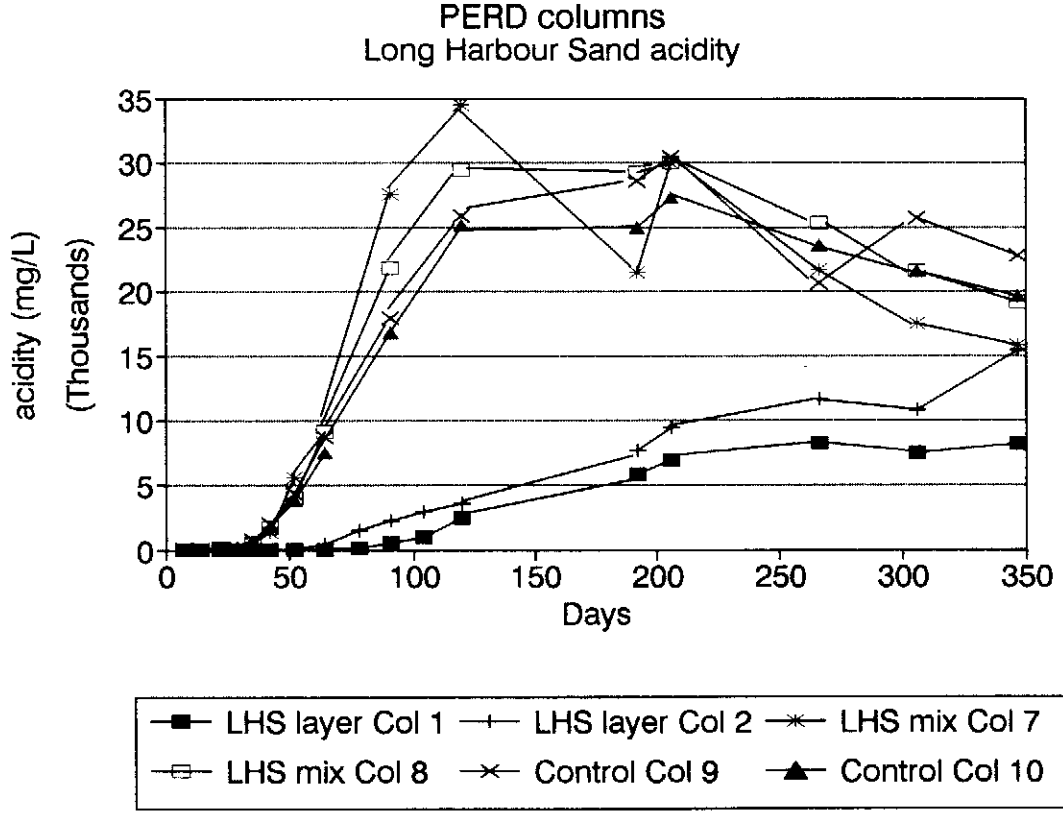


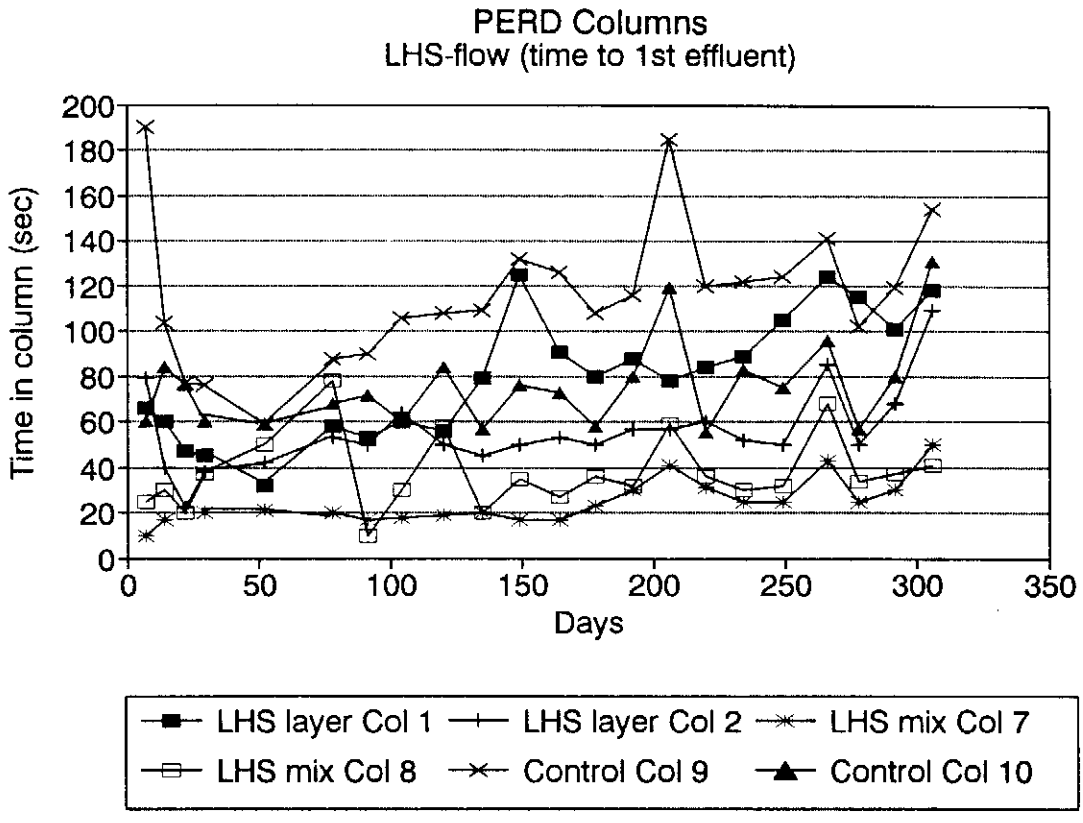
PERD Coal Columns
Redox Potential (Eh)

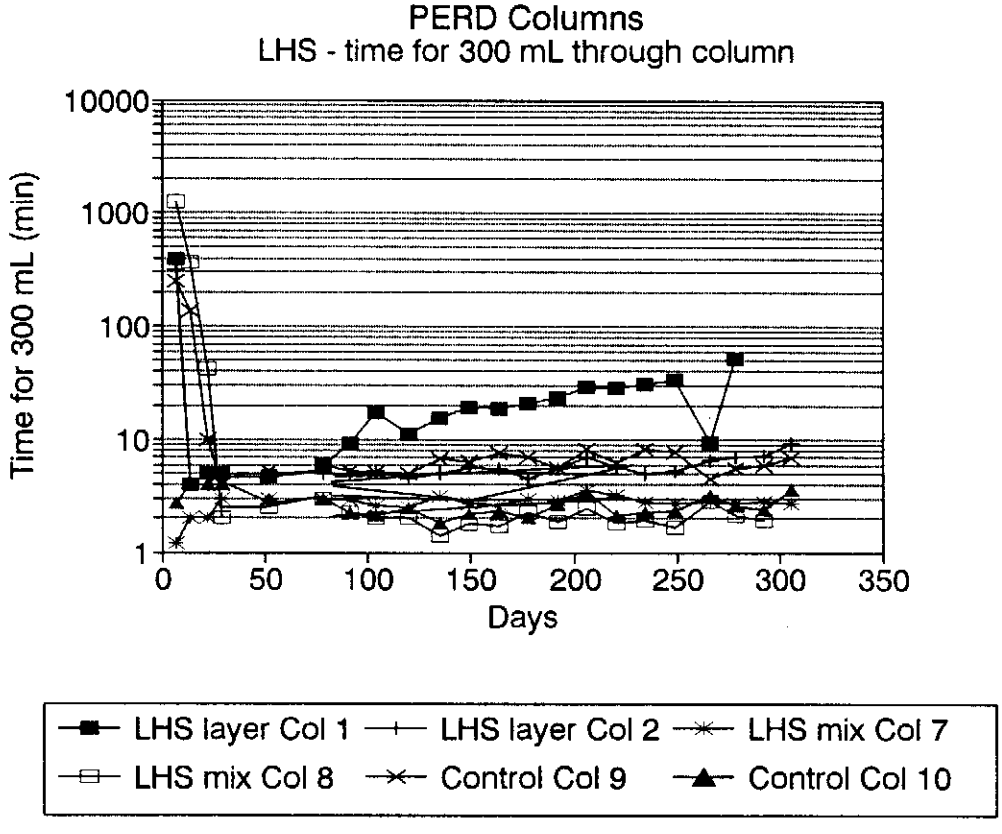


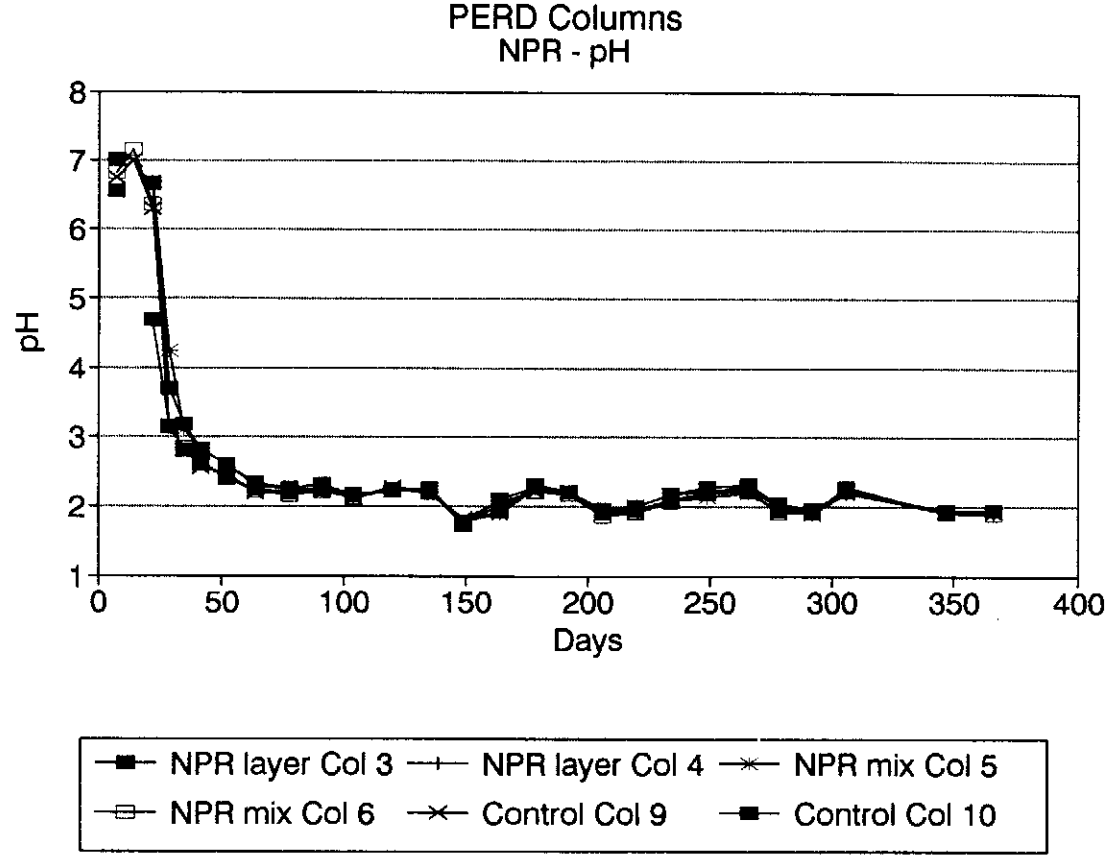


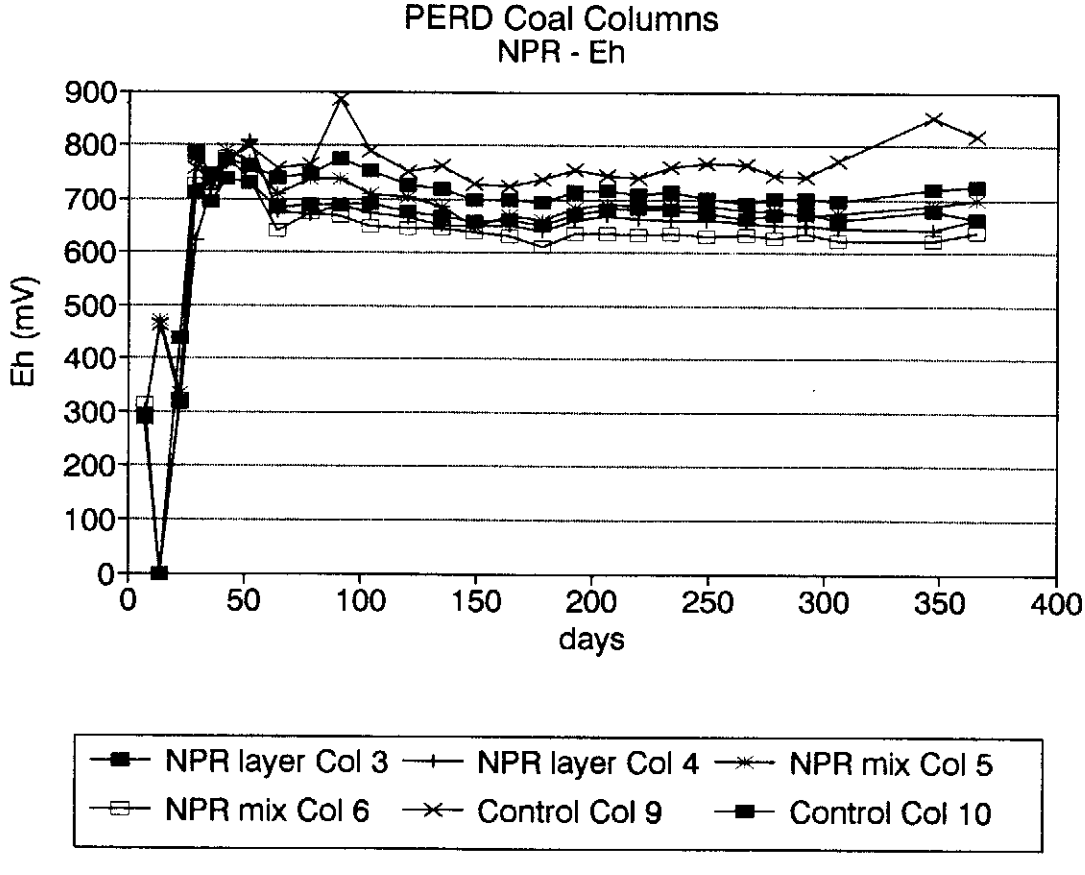

PERD Coal Columns
Long Harbour Sand-Conductivity
Conductivity (umhos/cm)
(Thousands)
16
14
12
10
8
6
4
2
0
50
100
150
200
250
300
350
400
days
LHS layer Col 1
LHS layer Col 2
LHS mix Col 7
LHS mix Col 8
Control Col 9
Control Col 10

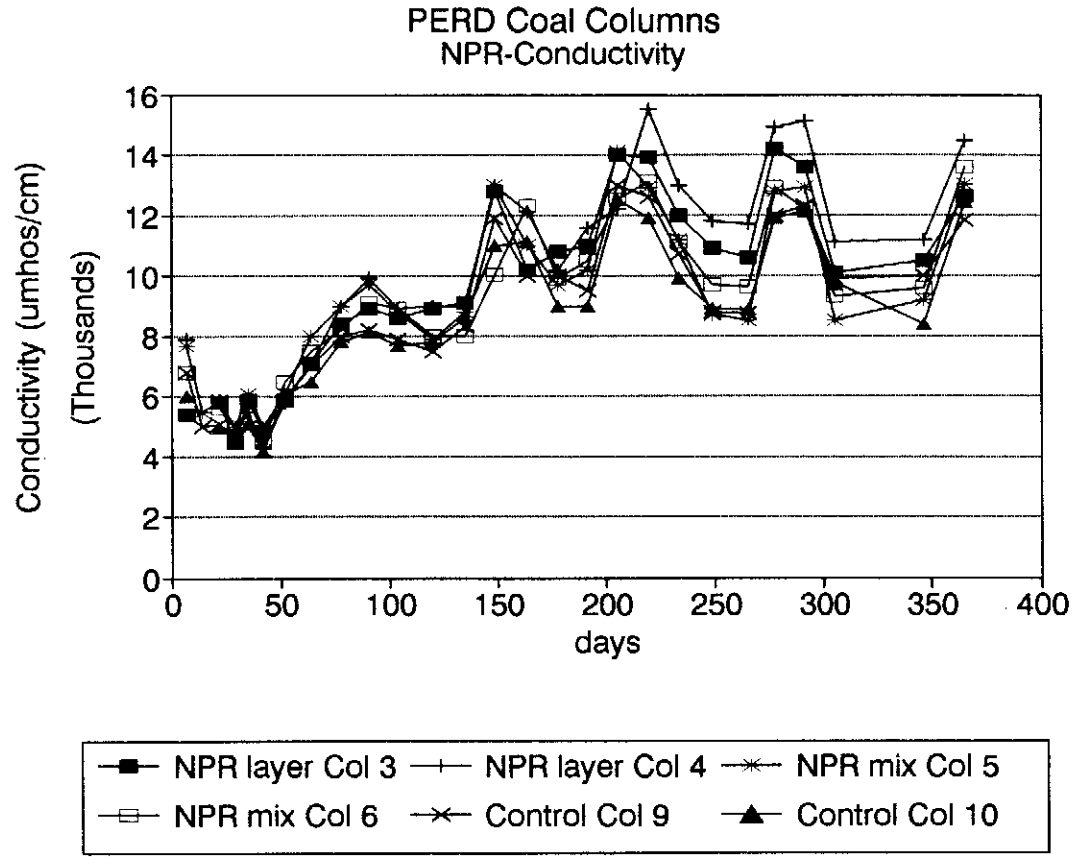

PERD columns
Long Harbour Sand acidity
acidity (mg/L)
(Thousands)
35
30
25
20
15
10
5
0
0
50
100
150
200
250
300
350
Days
LHS layer Col 1
LHS layer Col 2
LHS mix Col 7
LHS mix Col 8
Control Col 9
Control Col 10

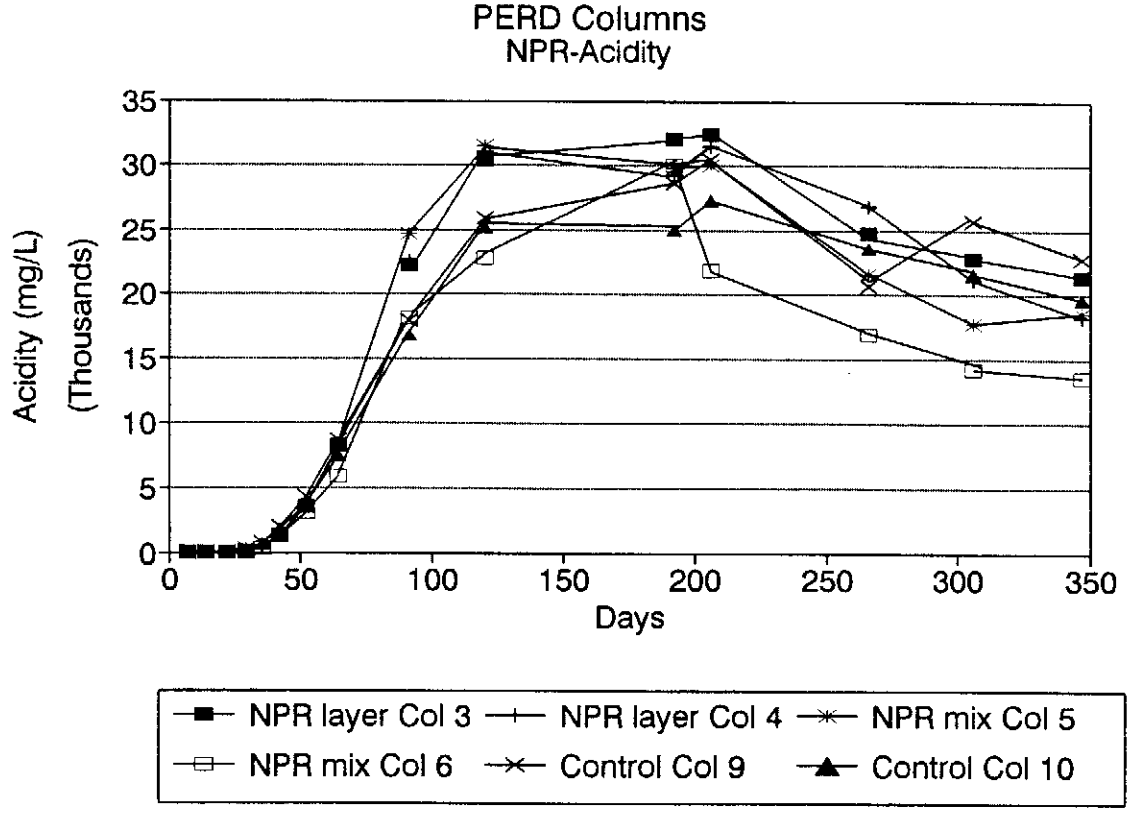

PERD Columns
LHS-flow (time to 1st effluent)
Time in column (sec)
200
180
160
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
Days
LHS layer Col 1
LHS layer Col 2
LHS mix Col 7
LHS mix Col 8
Control Col 9
Control Col 10


PERD Columns
LHS - time for 300 mL through column
Time for 300 mL (min)
10000
1000
100
10
1
0
50
100
150
200
250
300
350
Days
LHS layer Col 1
LHS layer Col 2
LHS mix Col 7
LHS mix Col 8
Control Col 9
Control Col 10

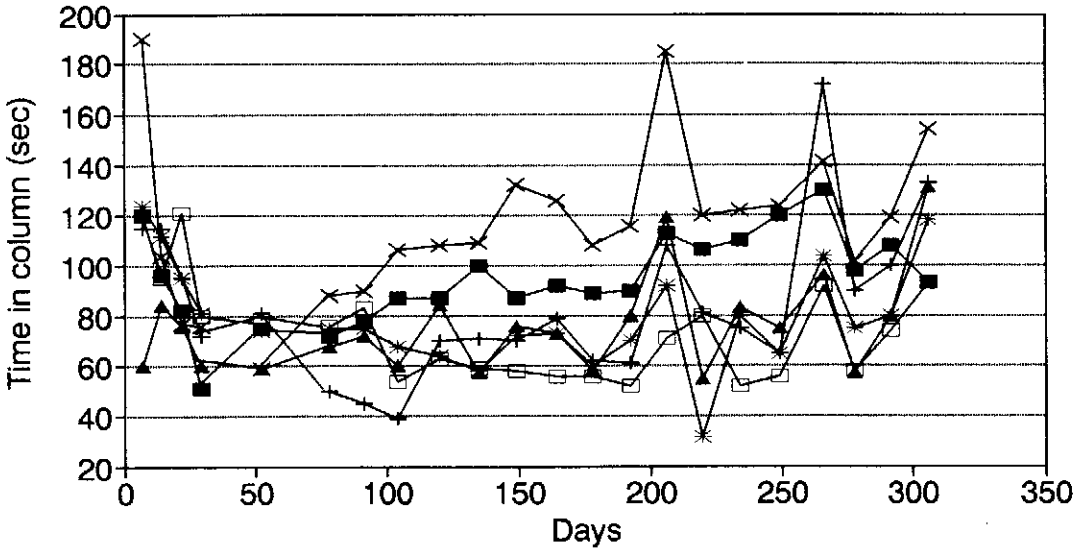

PERD Columns
NPR - pH
pH
Days
NPR layer Col 3
NPR layer Col 4
NPR mix Col 5
NPR mix Col 6
Control Col 9
Control Col 10


PERD Coal Columns
NPR - Eh
Eh (mV)
days
NPR layer Col 3
NPR layer Col 4
NPR mix Col 5
NPR mix Col 6
Control Col 9
Control Col 10


PERD Coal Columns
NPR-Conductivity
Conductivity (umhos/cm)
(Thousands)
16
14
12
10
8
6
4
2
0
0
50
100
150
200
250
300
350
400
days
NPR layer Col 3
NPR layer Col 4
NPR mix Col 5
NPR mix Col 6
Control Col 9
Control Col 10

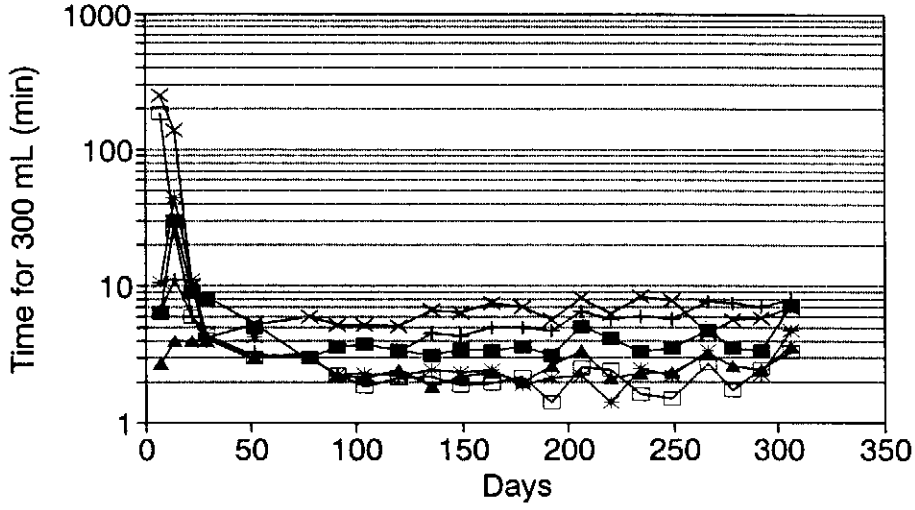

PERD Columns
NPR-Acidity
Acidity (mg/L)
(Thousands)
35
30
25
20
15
10
5
0
0
50
100
150
200
250
300
350
Days
NPR layer Col 3
NPR layer Col 4
NPR mix Col 5
NPR mix Col 6
Control Col 9
Control Col 10

PERD Columns
NPR-Flow (time to 1st effluent)



NPR layer Col 3 — NPR layer Col 4 — NPR mix Col 5
NPR mix Col 6 — Control Col 9 — Control Col 10

PERD Columns
NPR-Time for 300 mL through column



NPR layer Col 3 — NPR layer Col 4 — NPR mix Col 5
NPR mix Col 6 — Control Col 9 — Control Col 10

APPENDIX 2

NRC PROGRESS REPORT-MARCH 1993

PERD COAL PILE EXPERIMENTS-APRIL 1993

NRC PROGRESS REPORT-JANUARY 1994

Boojum RESEARCH LIMITED

HYDROLOGICAL AND MICROBIOLOGICAL RESEARCH IN SUPPORT OF AMD PREVENTION FOR WASTE ROCK AND TAILINGS

PROGRESS REPORT No. 1

for NRC IRAP

Project No. 22643U

March 1993

468 Queen St. East, Ste. 400, Box 19, Toronto, Ont. M5A 1T7 (416) 861-1086 Fax (416) 861-0634

SUMMARY

In the first phase of the project we focused our attention on methodological aspects of the ongoing waste rock experiments and we have commenced a critical review of the published work on phosphate rock uses with AMD material.

In the ongoing waste rock experiment, waste rock from a base metal mine which has experienced different degrees of weathering, had been set up in drums at Boojum Research outdoor facility 6 months ago, with two applications types of phosphate rock. The objective of this experiment is to develop a methodology to inhibit acid mine drainage from waste rock, through the formation of secondary minerals on the pyrite surface. The NRC project assists in assembling the SEM, EDX data, which will provide proof of coating of the pyrite surface.

Rocks from a waste rock leach which stop producing Cu in leachate (Gibraltar) are used as a reference in the SEM investigations of the waste rock surfaces. The secondary minerals on the Gibraltar rock appear to contain phosphate, suggesting that the correct approach is being taken. The effluents from the drums with the waste rock show marked differences in the acid generated since the experiment was set up. Differences are noted with respect to the application mode of the phosphate rock and compared to the control, i.e. rocks without phosphate rock.

The project should proceed to its second phase, as INCO and Denison Mines have committed to set up a field test plot, although MEND approval has been delayed, due to an overall review of the projects funded in the Prevention and Control section of the joint industry and Government program. We have received tailings from INCO and are collecting background information on the material for the test plot design.

The market potential of the proposed technology development has been revisited and an estimate is given for increases in Boojum's gross revenue.

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1.0 Literature review: The use of phosphate rock in AMD material

Preventive measures for the inhibition of acid generation have to consist of two key components. Firstly the oxygen has to be consumed which is required for the microbial oxidation of the pyritic material. Secondly, the acid which has been produced on the surface of the pyrite has to be neutralized, which would be best achieved in the immediate vicinity in which the acid is generated, namely on the pyritic surface. The proposed test plots on INCO (Base metal) and Denison (Uranium) tailings will incorporate oxygen consuming bacteria in organic matter in the root zone of a vegetation cover. Phosphate rock will be incorporated into the tailings to neutralize the acid already generated (carbonate component of the phosphate rock) and to provide slow release neutralization on the surface by dissolving phosphate component of the material.

Phosphatic material has been tested mainly with coal refuse as a neutralizing agent. The work which has been published to date is reviewed with respect to the preventive nature of the material.

Reclamation Research Unit-Montana State University, 1990. E. Spotts, D.J. Dollhopf Evaluation of Phosphate Sources for Control of AMD in Coal Overburden. pp 1-69.

"... concentration of free Fe^{+3} and its ability to oxidize FeS_2 is dramatically reduced by the addition of a source of phosphate ions (PO_4^{-3}). Phosphate is effective in this regard because it can precipitate the Fe^{+3} ion in a relatively insoluble form as a $FePO_4$. It can also precipitate Fe^{+2} as $Fe_3(PO_4)_2$ rendering it unavailable for oxidation to Fe^{+3}, either by bacteria or oxygen. In addition the iron phosphates can precipitate on the surface of FeS_2 crystals, further limiting FeS_2 reactivity" (pg. 17).

This statement of the authors indicates the preventive and neutralizing usage of phosphate. However no evidence is given that oxidation of the phosphate precipitate may not take place. The literature has to be evaluated from the microbial point of view and the oxidation of reduced iron precipitates has to be evaluated chemically, to confirm or refute the statement made.

"... apatite was more effective in controlling acid production than either sodium lauryl sulfate or limestone. In addition, the rates of apatite required to effectively control acid production were approximately five times less by weight than the amount of limestone needed, indicating that the use of apatite for the control of AMD may be considerably less expensive than a similar use of limestone, assuming both sources are readily available" (pg. 17&18).

Comparing apatite to limestone or the sodium lauryl sulfate as agents controlling acid generation is inappropriate based on the effects which can be expected from these different products. Limestone can only neutralize acid which is already generated. Sodium lauryl sulfate is a bactericide (surfactant) which would kill the oxidizing bacteria, resulting in a slower rate of acid generation. Apatite has two functions, neutralization due to the carbonate component and formation of iron precipitates on the surface of the rock.

The rates of application are stated to be five times less by weight than limestone. This is partly a function of the density of the material. The density of limestone (2.6 to 2.7, Handbook of Physics and Chemistry) is higher than that of apatite which is 1.6 (Texas Gulf-specification of Code 30). Limestone will only neutralize the acid generated and will not inhibit acid generation. Therefore in order to assess the application rates of limestone and phosphate rock (apatite), the following considerations have to be made.

The application rate for limestone is a function of the total acidity which has been generated from the AMD material and also of the acid generating potential of the material ie. the total acid mine drainage which could be generated from the material. For phosphate rock, the application rate will depend on the acid already generated in the material and the metal concentrations, particularly iron, available to form precipitates. The effectiveness of the inhibition will largely be a function of the contact of the solubility products of apatite and its formation of secondary minerals on the pyrite surface.

The statement on the economics is not substantiated, since it does not consider a $ value for reduction (the inhibition of the acid generated). The shipping costs, have to be evaluated with respect of costs per tonne of alkalinity which can be generated from the material. Since phosphate rock is denser, the economics of shipping should be evaluated based on the amount of alkalinity per tonne shipped and the amount of iron precipitation material per tonne shipped, not taking into account either bulk cost of medium or transport.

"... the insolubility of apatite above pH of approximately 4.5 insures that PO_4^{3-} ions will be available as an in situ, point source control of AMD until the pH drops to this value. At this point the dissolution of apatite renders PO_4^{3-} ions available for the precipitation of iron. At this point, the dissolution of hydroxy apatite also liberates hydroxyl groups into solution, providing a source for H^+ neutralization" (pg.18).

The solubility of apatite depends on the pH of the solution and in principle it is not insoluble. At pH 7 the following reaction will take place:

$$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{+2} + 2PO_4^{-3}$$

and at pH 4.5 the following reactions will occur:

$$Ca_3(PO_4)_2 + 2H^+ \rightleftharpoons 3Ca^{+2} + 2HPO_4^{-2}$$

$$Ca_3(PO_4)_2 + 4H^+ \rightleftharpoons 3Ca^{+2} + 2H_2PO_4^-$$

The rate at which these reactions will take place is also different, i.e. at higher pH lower reaction rates and at lower pH higher dissolution rates can be expected. The effectiveness of apatite as an inhibitor of acid generation, lays in the production of precipitates with iron below pH 4.5 and therefore in the contact with the acid generating source, i.e. the pyritic surface where pH is always low.

Providing the correct mixing conditions is one of the main reasons for the proposed test plots. There is a wide range in particle size of the uranium tailings, base metal tailings and the waste rock. The application methods will be those used in general tailings reclamation, where INCO agriculture has extensive expertise.

"The performance of the Texas Gulf ore at 3% application rate was not markedly better than The Stauffer sludge at 5% rate of application. Although it achieved the most significant reductions in acidity, Stauffer sludge at 5% was just as effective at reducing Fe levels and both initial (cycle 1) and cumulative S concentrations. Since it was not the objective of this study to evaluate the feasibility of the use of the Texas Gulf ore as an amendment in the western United States, this issue will not be addressed. However, the performance of the Stauffer sludge relative to this source is encouraging, especially in light of the results of previous research (Renton 1988, The use of Phosphate Materials as Ameliorants for AMD. Mine Drainage and Surface Reclamation, Conference in Pittsburgh, Pensylvania, pp 67-75), which had determined the Texas Gulf ore to be a very effective source of phosphate at controlling acid production relative to other sources tested" (pg. 58).

Other sources of phosphate were: Cominco ore (apatite mined from the Permian Phosphoria Formation near Garrison Montana), Cominco waste (byproduct of the washing of crushed ore - Garrison), Stauffer ore (apatite mined from Permian Phosphoria Formation in southeastern Idaho), Stauffer sludge (dried slurry material being byproduct of elemental phosphate production), Triple Super Phosphate

(commercially available calcium phosphate fertilizer) and Texas Gulf (processed apatite rock).

It is of more than passing interest to recognize that different materials in this work produced different results. This is likely due to the fact that the solubility changes with respect to mineralization and processing of the material. The reaction kinetics are related to surface area (different grinds are being tested presently, to design the test plots) and processing. A calcined phosphate rock reacts much faster than non-calcined product.

P.F. Ziemkiewicz et al., 1990. Advances in the prediction and control of AMD. IN: Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Vol. 1, Charleston W. Virginia, 1990, pp 93-101

"It should be also stressed that phosphate is not being used as a neutralizing agent. Application of phosphate to mine refuse rock surfaces creates a physical and chemical environment which prevents the formation of acid. Iron ions from pyrite grains are prevented from reacting with water and oxygen by participating in a faster reaction with the phosphate anions. Subsequent precipitation of insoluble iron phosphate salts may further inhibit availability of reacting pyrite sites. Neutralizing agents such as limestone, on the other hand, permit the oxidation of pyrite to occur and than react with the products. This is why massive amounts of neutralizing agents are required to control AMD. It is unlikely that addition of low ratios of phosphate to already oxidized rock will have much beneficial effect" (pg.94).

This point of the author stresses the difference between limestone and phosphate rock as an approach to the preventive advantages and also stresses that phosphate should not be considered only as neutralizing material.

"... The effectiveness of rock phosphate in controlling AMD production has been demonstrated in both laboratory and small scale field trials" (pg. 96).

The full scale application has to be tested. To our knowledge the full scale applications were not carried out due to economic considerations. However it was not possible to date to ascertain details which lead to this decision.

Tech-Talk. Review of latest 'new technology' publications. Canadian Mining Journal, February 1993, pp 21-23.

It is stated in the review of the book by R.K.Singhai, Environmental issues and management of waste in energy and mineral production. A.A. Balkema Publishers, Brookfield, Vt. 1487 pp. that: " Scientists at the University of Kentucky, for example, report here on a permanent, cost effective way to prevent pyrite - one of the main culprits in AMD in coal wastes -from oxidizing. The technique involves coating pyrite with a relatively inert ferric phosphate. " The coatings shut off electron transfer between pyrite and oxidizers necessary for oxidation", Says Bill Evangelou and Ziao Huang of the university.

This statement, by a preeminent acid mine drainage chemist is confirming the proposed inhibition role of phosphate rock, in the application to be developed.

A. F. Meek Jr., (1991). Assessment of acid prevention techniques employed at the Island Creek Mining. IN: Twelfth Annual West Virginia Surface Mine Drainage Task Force Symposium, April 1991, pp 1-9.

" As shown, the most cost effective acid preventive technique employed at the Upshur Complex was selective handling and placement with phosphate/apatite admixed technique.

In the conclusion, it can be said that none of the techniques attempted were entirely successful in the complete elimination of AMD" (pg 7).

The phosphate was compared with: selective placement, selective placement with PCV liner, selective placement with lime, and proved to be the most economically viable. The pilot scale experiment results are based on 6 years of observation. It is not unreasonable to expect, that complete inhibition was not achieved, since the optimal mixing and type of apatite would have to be determined, prior to the field tests.

Paul F. Ziemkiewicz, Jeffrey G. Skousen, 1992. Prevention of Acid Mine Drainage by Alkaline Addition. IN: Proceedings of the 13th Annual W.Virginia Surface Mine Drainage Task Force Symposium, 10 pp.

" The results indicate that at least under laboratory conditions, a ratio of neutralization potential to maximum potential acidity (NP/MPA) of 0.35 or greater resulted in neutral to alkaline leachate" (pg.1).

"Supporting the latter contention is the NP/MPA ratio at which AMD is controlled in laboratory tests. For kiln dust and FBC ash the ratio was 0.35 or greater. Phosphate was lower in two cases, generating neutral drainage (e.g. greater than 6.0) with ratios of 0.18 (samples 8078 and 8096). The NP of the rock phosphate **used in this study was only 0.14** (measured NP expressed in percent calcium carbonate equivalent for each of the amendments were: kiln dust 99%, FBC ash 26%, phosphate 14% - pg. 7), suggesting that at least some of its effect on acidity reduction may stem from precipitation of iron phosphate. Except for these two phosphate treatments, every sample which had an NP/MPA ratio of 0.35 or greater generated neutral drainage" (pg. 7).

In this work the phosphate amendment is at a disadvantage because of the experimental design. The experiment compares materials which are assumed to mitigate AMD in differentways yet draws conclusions based purely on neutralisation potential (NP).

AMD neutralization by kiln dust would be more effective since it is readily soluble and contains 99% equivalent of calcium carbonate. The authors have already stated in 1990, that phosphate use for neutralization would unlikely be beneficial, as it should not be considered as a limestone substitute or neutralization agent alone.

"Other alkaline materials has higher NP's than calcite. Quicklime, kiln dust, and hydrated lime all have higher activities than calcite, though it is not clear that the kinetics of pyrite oxidation favour readily soluble sources of alkalinity" (pg. 3).

The kinetics of interaction between phosphate and refuse is quite different from that of the other amendments used in the experiment.

"To be an efficient process, the acid-forming and alkaline rock must be thoroughly mixed. This largely becomes a materials handling issue" (pg. 4).

In the tailings pile, acid is mostly generated in the vadose zone. It is not realistic to expect to mix the phosphate rock into the entire tailings deposit to achieve a mixture which would facilitate contact between the pyrite surface and the apatite. The proposed tailings cover applications integrate the material only in the upper surface of the tailings pile and at the same time promote the growth of oxygen consuming bacteria.

"The data, **excluding** the phosphate data, were used to develop a simple curvilinear regression model to predict pH on the basis of NP and MPA" (pg. 8). **It would be interesting**

to include phosphate results into the prediction model and no explanation is offered why these data where omitted.

In conclusion, the reviewed papers do not provide any evidence, which would suggest that the proposed use of the phosphate rock, together with the oxygen consuming bacterial growth in the root zone should not result in a successful reduction of acid generated.

2.0 Market Potential

A technology which would facilitate a reduction in acid generation from pyritic waste products would be in great demand. All mining companies are seeking economically acceptable means of reducing acid generation. At present, cost-estimates for tailings covers alone, for an average base metal operation with 6,000 tpd production, ranges between $10 and 20 million and for waste rock, between $10 and 50 million for tailings.

These covers do not prevent or reduce acid mine drainage, they merely reduce infiltration of precipitation, which in turn reduces the volume of effluent to be treated. In Table 1, a summary is provided of the areas which can be expected to produce acid mine drainage. These data are estimated by Boojum Research and they agree reasonably well with other published areas, given in annotations.

If we assume that the cost of treating 1 m^3 of acid mine drainage is estimated to range from $0.2 to 0.6 (Kilborn, 1991) and the annual base flow in Canada can be expected to produce about 44 million m^3 of contaminated water (Table 1) the annual lime expenditures alone of the sector are at least $88 million. As this treatment is required in perpetuity, it would not be unreasonable to expect to set a price for the technology which could be estimated in the order

of 9 millions divided by the total amount of ha generating acid area, would result in a increased cost of the preventive cover of $ 1,500/ha. Since the published rehabilitation costs for abandoned mines in Ontario and Quebec are in the order of $125,000/ ha (Filion and Ferguson, 1989) such an additional cost would not be unreasonable.

Operating mines have to post bonds in relation to their environmental liability in order to cover these decommissioning costs. If we assume that 10 mines are using the new technology in 3 to 5 years, the market value of the technology at 5% savings in AMD treatment costs and cover development would represent a significant market.
The decommissioning of mines is a regulatory requirement in Canada and in the United States. The owners of mines must post bonds with the regulatory bodies to ensure compliance with the decommissioning regulations. Some of these bonds are valued in the $100 million range, representing a high value liability for both the mining operation and the bonding company. The cumulative cost of treating AMD, a component of the overall decommissioning of a mine, is estimated at $4-6 billion over the next 15 years in Canada.

Assuming that Boojum Research can develop an inhibitive cover for tailings with the proposed technology and maintain a leading edge in the applications of the technology, the revenues to the company can be expected to increase dramatically and estimates of increasing the annual sales by $500,000 per annum may not be unrealistic.

Table 1
Estimated areas of sulphide tailings and waste rock,
volumes of AMD and sludges produced in Canada

Province/Territo	Precipitati	Tailings	Waste ro	Total area	Base flow	Sludge
	mm	ha	ha	ha	10^6 m3	10^6 m3
British Colombia	1016	780	625	1405	14.3	2.1
Alberta	508	no data	no data	no data	no data	no data
Saskatchewan	508	no data	no data	no data	no data	no data
Manitoba	550	1264	no data	1264	7.0	1.0
Ontario	780	916	125	1041	8.1	1.2
Quebec	762	932	0.6	932.6	7.1	1.1
New Brunswick	889	448	10	458	4.1	0.6
Nova Scotia	1016	no data	no data	no data	no data	no data
Newfoundland	762	no data	no data	no data	no data	no data
Yukon	711711	367	25	392	2.8	0.4
Northwest Terri	254	402	no data	402	1.0	0.2
Total	7756	5109	785.6	5894.6	44.3	6.6

Assumes 10 ha/tonne tailings
Assumes 2.5 ha/tonne waste rock
Assumes iron hydroxide sludge 15 % wt/volume

Monenco estimate (1984) 9000 ha
Murray (1977)satellite estimate of total tailings 17478 ha
of total waste rock 7157 ha

For tonnage refer to: The State of Canada's Environment, 1991

3.0 Waste Rock Experiment

3.1 Introduction

Waste rock dumps are significant sources of acid, generated by the oxidation of sulphides. Oxygen and water supply are oxidation rate-controlling factors, and oxygen supply is the reaction-limiting component.

If secondary minerals can be formed on the surface of the rocks, pyrite oxidation and therefore acid generation may be inhibited. Evidence for this notion comes from the Gibraltar waste rock pile, which was used as a heap leach for copper. Part of the heap ceased to produce either metals or acid. An investigation revealed that rocks were covered with secondary minerals which may have inhibited oxidation. Boojum Research has been investigating the use of Natural Phosphate Rock (NPR) as a phosphate based secondary mineralization initiating medium. A laboratory experiment was set up to:

1) Observe and analyze mineral precipitation on the surface of rock samples from Les Mine Selbaie (Gibraltar rock samples will serve as a reference and their cover composition will be analyzed as well).

2) Analyze microbially mediated oxidation on the pyrite surface.

3) Analyze acid generation in the presence of NPR; quantify acid generation as a function of a rock type.

A total of 17 drums with rock samples, were set up outside the Boojum laboratory, exposed to the ambient weather conditions. The waste rock in each drum is underlaid with a layer of styrofoam blocks to facilitate drainage. Sampling ports extend to the bottom of the drums. Overflow drains positioned at the styrofoam - waste rock interface have been installed to

remove excess water, so that waste rock overlies, but is not soaking in AMD.

Principal hypogene minerals in the waste rocks used in the experiment are: pyrite, sphalerite and chalcopyrite. Galena, tetrahedrite, polybasite and native silver are encountered in minor amounts; native gold in trace amounts. Host rock is comprised of dacite tuff and rhyodacite breccia. Samples were collected at Les Mines Selbaie in the spring of 1992. The stage of weathering, type and lengths of exposure, was confirmed with the mine chief geologist. The characteristics of the rock types are as follows:

Type A - low pyrite fresh waste rock, which was weathered for one winter (from the pit at the end of 1991 or early 1992).

Type B - high pyrite fresh, dumped within the months of collection.

Type C - low pyrite with high fraction of dacite tuff; weathered for 4 or more years.

Type D - essentially dacite tuff.

Type E - high pyrite old, low grade ore, weathered for 4 or more years.

Four drums were built for each type of rock, except for type D (one drum), which was classified as non-acid generating rock. In order to quantify the surface oxidation of the rocks, 99 rocks were cut; one-half of each rock was inserted into a drum containing the same type of rock. The other half is being stored in nitrogen, for comparison at end of the experiment. In addition, a thin section of each type of rock were also placed into the drums. Therefore, this experimental design results in the following configuration, where X (A, B, C, D, E) indicates the rock type.

Drum X-1, control drum without NPR, 1 thin section.

Drum X-2, treatment drum, net on the styrofoam support at the bottom of a drum (NPR throughout drum); cut samples in direct contact with NPR (3.6 L equivalent to 0.05 m layer).

Drum X-3, treatment drum, net approximately 0.30 m above the styrofoam support (NPR in top half of drum only), between rocks; cut samples below net (not in direct contact with NPR).

Drum X-4, prepared for treatment with spent NPR, which is not yet available.

Drum D-1 is a control drum, containing 30% of type C and 70% of type D rock. This ratio was provided by the chief geologist as the ratio representative of non-pyritic material to pyritic material which comes out of the pit. Hence, drum D-1 simulates the unsegregated waste rock. It will be used to assess the relative importance of non-acid-generating material in the waste rock pile.

The differentiation of the NPR treatment drums with the configuration X-2 and X-3 is dictated by the following considerations:

Waste rock piles consist of lifts, onto which NPR, used in the ditches is to be placed. The uppermost layer of each lift is very compacted, due to haul truck and bulldozer activity. Therefore, an assumption is made that the NPR, distributed as a thin layer (0.05 m) on top of the lift, would not trickle into the pile. By the time a NPR layer is placed on the surface of the final lift, the acid generation will have already started in the older lifts. Therefore NPR layers will react with neutral rain or snowmelt (top layer) and with acidic, metal contaminated waters (lower layers). AMD contacting NPR will be neutralized and a precipitation layer, will be formed. The X-2 and X-3 configuration will address:

X-2: NPR treated water, carrying phosphate, carbonate and sulfate precipitate on the surface of cut samples; direct contact NPR-cut samples (Schematic 1).

X-3: metal contaminated water of higher (compare to X-3) acidity reacts with the phosphate, carbonate and calcium; formation of precipitation layer on the rock surface, no direct contact NPR-cut samples (Schematic 1);

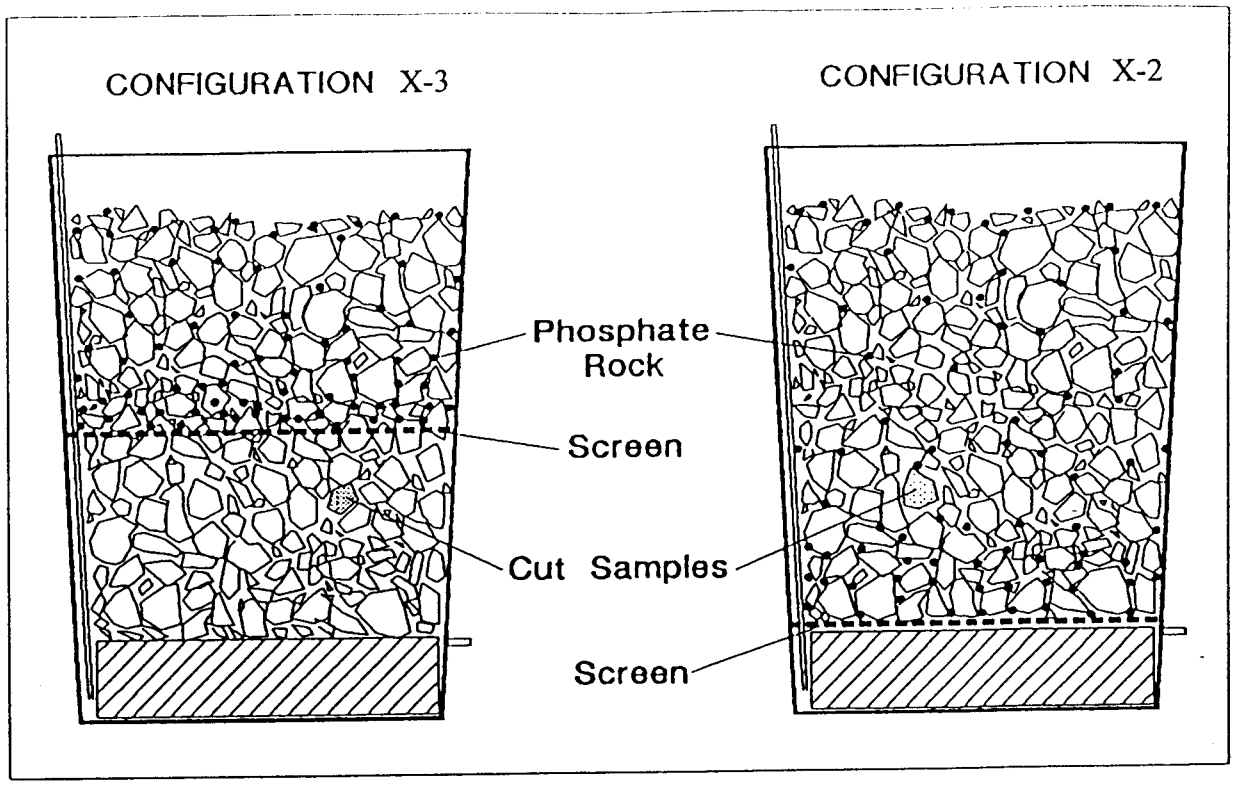
Void ratios of rock in each drum were determined and are given in Table 2. The void ratio represents the ratio of the volume of water drained from a drum filled with rocks, to that of the bulk volume occupied by rocks. The ratios achieved for all 17 drums were a minimum of 41.2, and a maximum of 47.8, a relatively narrow range.

3.2 Experiment maintenance

In January 1993, an additional drum was set up with phosphate rock alone to measure alkalinity generation from 3.6 L of NPR receiving neutral precipitation. At the same time this drum will enable us to determination the total amount of water "processed" by drum between measurements.

3.3 Experiment monitoring

Since the beginning of the experiment (August 25,1992), ten sets of measurements had been made. During that time the following sampling and observation procedure was developed:



Schematic 1: Location of phosphate rock layer in drums.

Table 2: Waste Rock Experiment

Void Ratio

Drum#	h cm	V2 L	V3 L	RATIO V3/V2	RATIO %
A-1	14.2	48.29	20.00	0.41	41.42
A-2	13.7	49.04	21.70	0.44	44.25
A-3	15.1	46.94	20.50	0.44	43.67
A-4	12.2	51.30	23.30	0.45	45.42
B-1	13	50.09	22.80	0.46	45.52
B-2	10.7	53.58	25.65	0.48	47.87
B-3	12.9	50.24	21.80	0.43	43.39
B-4	11.43	52.47	22.23	0.42	42.36
C-1	15.3	46.65	21.80	0.47	46.73
C-2	13.4	49.49	21.60	0.44	43.65
C-3	15.4	46.50	20.00	0.43	43.01
C-4	13.6	49.19	21.80	0.44	44.32
D-1	14	48.59	21.20	0.44	43.63
E-1	13.8	48.89	22.20	0.45	45.41
E-2	11.2	52.82	23.20	0.44	43.93
E-3	8.7	56.65	25.48	0.45	44.98
E-4	11.2	52.82	23.30	0.44	44.12
AVG					44.33

Note:

Dimensions of each drum:
High [cm] 50.00
Top radius [cm] 22.70
Bottom Radius[cm] 19.62
h - distance [cm] to water leve
V - Total volume of the drum [82.16
V1 - Used volume of the drum 70.40
V2-Volume of the water and rocks[L] V2=V2(h)
V3 - Volume of drained water [L]

Outside measurements

Temperature: daily basis using min-max thermometer.
Precipitation: daily basis using rain gauge.
Outflow from a drum by measurement of water retained in the 5 gallon plastic container at the outflow of NPR alkalinity drum. Done at each drum-sampling day.
Relative humidity: daily basis(noon) using a sling psychrometer.
For the period September 1992-March 1993 data were recorded at the Toronto City (downtown) station operated by Environment Canada. Since December the Boojum Meteorological Station has been operating.

Water sampling.

Samples were taken approximately every two weeks except when the drums were frozen. In this case, sampling was carried out on the first day following thawing.
At each sampling, 250 mL of water was taken from each drum through the sampling pipe. Additional samples are taken from a rain water bucket and from the NPR alkalinity drum.

Laboratory processing.

Samples are processed on the same or on the following day. Titration for alkalinity and acidity are done using a Metrohm SM 702 Titrino autotitrator. Additional measurements include pH (Jenco 672), Eh and electric conductivity by standard methods. Samples from December 18, 1992; January 05 and January 22 1993 were filtered, acidified and stored for future chemical analyses.

3.4 Results

Results are presented for the samples collected from Sept. 1992 to Mar. 1993.

Cumulative acidity

Eventually acid generation by drums will be related to rock surface area, pyrite content etc. To this point, acidity and alkalinity of discharge water per drum have been determined.

Cumulative acidity (equivalent of mg $CaCO_3$/drum) is calculated as total acidity discharged from drum and is equal to:

(1) Generated acidity (mg $CaCO_3$/L) x volume of water discharged from drum between measurements (L) + previous cumulative acidity

If a drum is not generating acid, but is still discharging water as a result of precipitation or melting, then the resultant acidity of discharged water will be proportional to dilution of reservoir water (x acidity at previous measurement) and is referred to as expected acidity. Therefore, generated acidity (equation 1) is equal to:

(2) Measured acidity (mg $CaCO_3$/L) - Expected acidity (mg $CaCO_3$/L)

The slope of cumulative acidity curves represents the acid generation rate of a drum. Measured acidity for each drum is shown in Table 3.

Figure 1 shows the cumulated acidity discharged from control drums (no NPR) of each rock type. The initial high rates in these and in the other drums may be partly attributed to acidity generated on the rock surfaces prior to their placement in the drums. The drums with low pyrite weathered rock (C1) and mixed rock (D1) generated approximately five times as much acidity as drums with the other rock types. The 5:1 ratio was maintained through the observation period.

Figure 2 and 3 shows cumulated acidity for drums with NPR. As for the control drums, much less acidity was generated from the weathered, low phosphate rock than from the fresher materials except for drum E3 (high pyrite, weathered rock) which showed high rates of acid generation, particularly towards the end of the study period.
Figures 4, 6, 8 and 10 show cumulative acidity for the 4 rock types. For all types except the high pyrite, weathered rock (type E) the control drum has generated the highest cumulative acidity generally 3 to 5 times as much as with NPR in the top of the drum and 6 to 11 times as much as with NPR throughout the drum. The NPR treatments are reducing acidity production considerably and the distribution of NPR throughout the rock column is the more effective NPR configuration. Direct contact or near presence of NPR is clearly necessary to optimize the reduction in acidity generation at this stage of the experiment.

Figures 5, 7, 9 and 11 show cumulated alkalinity for the 4 rock types. Very little alkalinity was generated in the absence of NPR. Drums with NPR throughout generated more alkalinity than those with the same amount of NPR confined to the upper half. Unlike acidity, alkalinity generation rate was steady for most of the study period for the fresh rocks (types A and B). For the weathered rocks with NPR in the upper half of the drum, alkalinity was produced for only the first 85 days of the experiment. With NPR throughout the rock column, these weathered rock produced alkalinity for longer.

Figures 12 and 13 depict changes in precipitation and temperature in the first 150 days of the experiment (from August 25, 1992). In general, the acid generation decreases with decreasing temperature. In the case of precipitation, a relationship is not apparent yet.

Table 3

Measured acidity

Drum	A1	A2	A3	B1	B2	B3	C1	C2	C3	D1	E1	E2	E3
Date													
22-Sep-92	132.5	16	27	114	18.5	24	614	67	173	587	130	11	68
01-Oct-92	270	17	30	191	22	32	1000	57	182	687	207	12	74
23-Oct-92	231.4	28	58.5	161.9	27.6	51	1093	112.2	231.1	1018	229.5	16.8	68.6
18-Nov-92	90.5	12.3	22.5	86.1	18.8	46.1	662.5	62.2	130.7	564.8	103.4	6.7	120.3
03-Dec-92	97.5	13.6	25	90.4	18.5	60.4	669.3	59.7	125.9	448	108.8	12.5	231.3
18-Dec-92	60.3	7	10.6	36.2	8	29.9	340.8	34.7	65.7	106.2	69.2	4.7	168.7
05-Jan-93	75	10.8	12.8	54.6	17.6	45.2	324.1	30.5	80.2	250.6	81.1	8.5	161.5
22-Jan-93	56.8	3.2	6.6	58.3	5.7	22	157	14.9	61.9	141.1	77.8	4.1	129.9
08-Mar-93	96.6	5.4	12.8	43.8	5.4	30	228.2	14	101.5	338.7	77.6	4.1	464.9
25-Mar-93	54	4.8	12	39.4	3.7	18.3	218.9	15.6	65	65.7	42.8	4.4	172.9

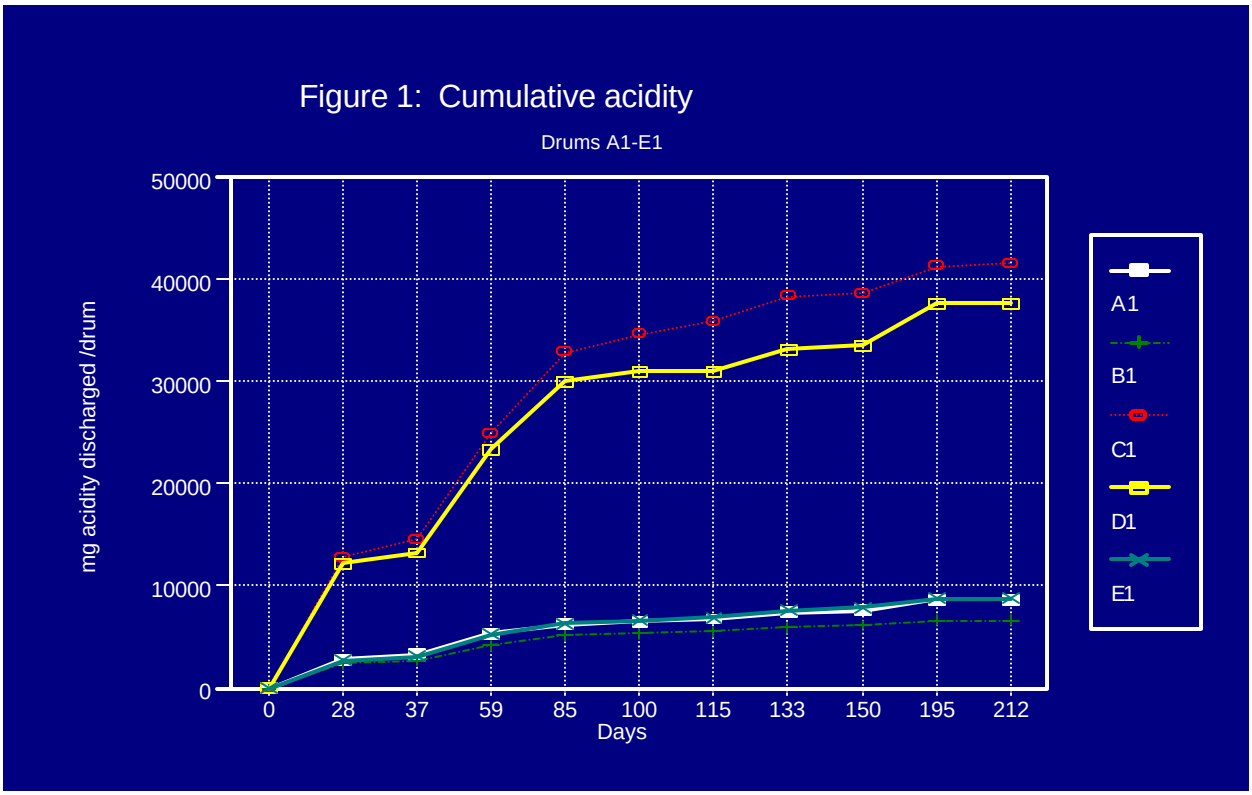


Figure 1: Cumulative acidity
Drums A1-E1
mg acidity discharged /drum
50000
40000
30000
20000
10000
0
0
28
37
59
85
100
115
133
150
195
212
Days
A1
B1
C1
D1
E1

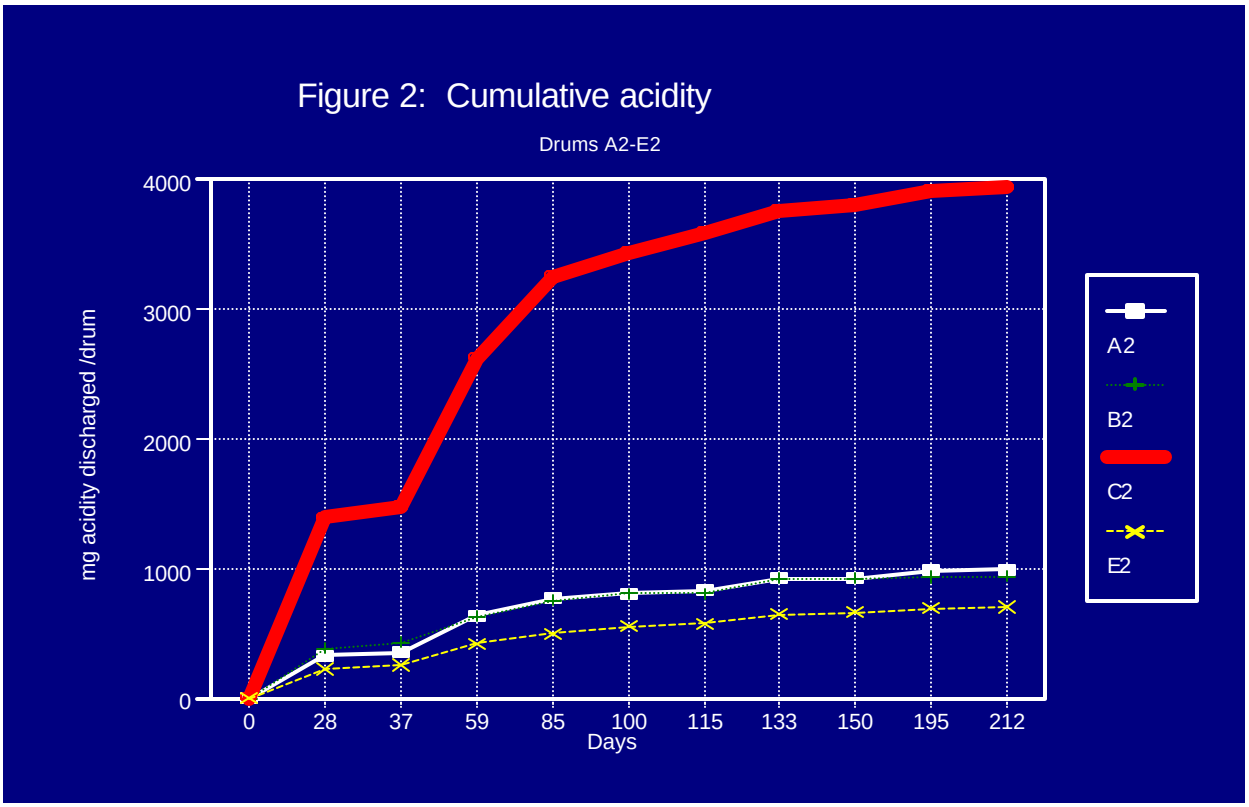


Figure 2: Cumulative acidity
Drums A2-E2
mg acidity discharged /drum
4000
3000
2000
1000
0
0
28
37
59
85
100
115
133
150
195
212
Days
A2
B2
C2
E2

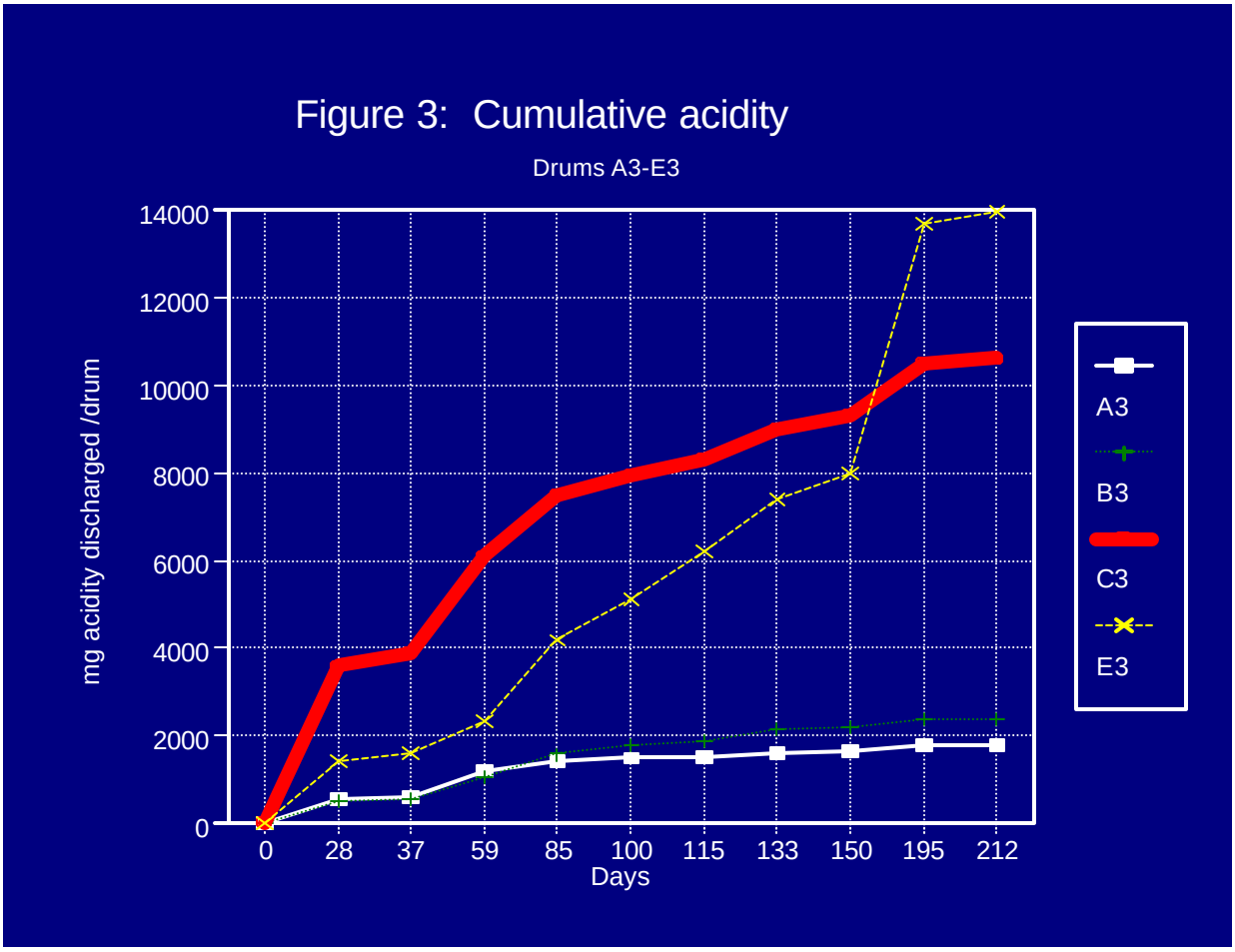


Figure 3: Cumulative acidity
Drums A3-E3
mg acidity discharged /drum
14000
12000
10000
8000
6000
4000
2000
0
0
28
37
59
85
100
115
133
150
195
212
Days
A3
B3
C3
E3

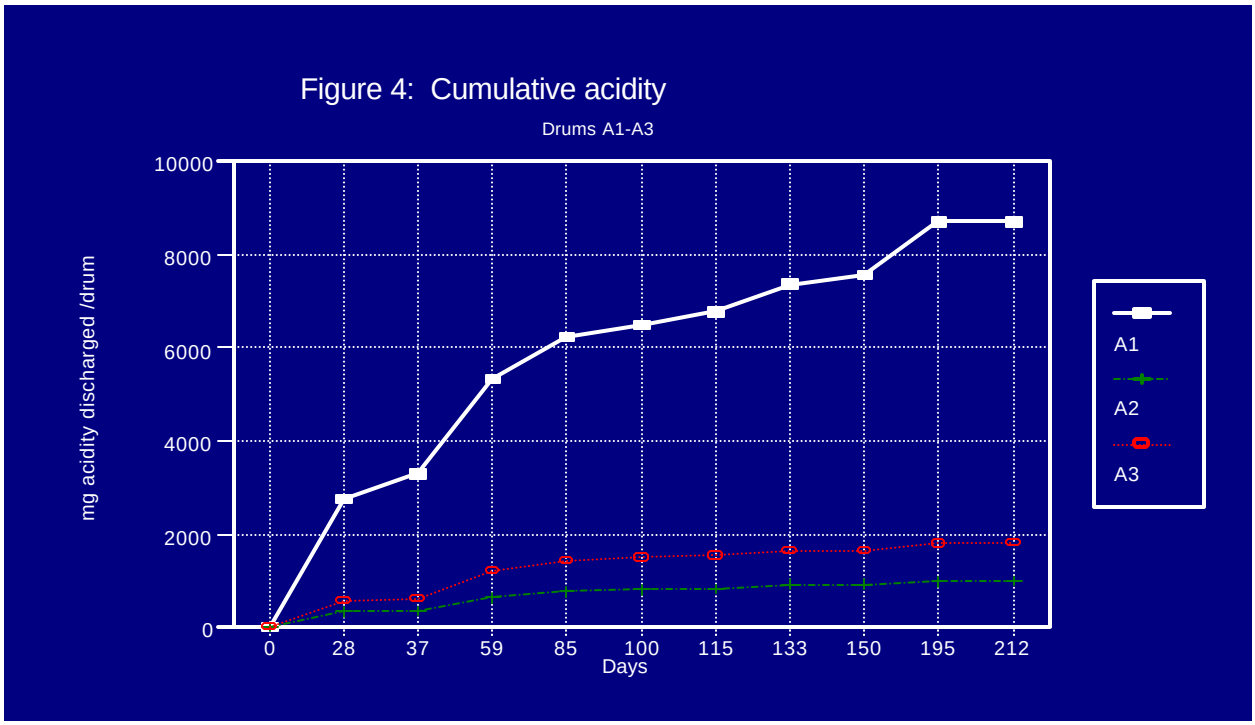


Figure 4: Cumulative acidity
Drums A1-A3
mg acidity discharged /drum
10000
8000
6000
4000
2000
0
0
28
37
59
85
100
115
133
150
195
212
Days
A1
A2
A3

Figure 5

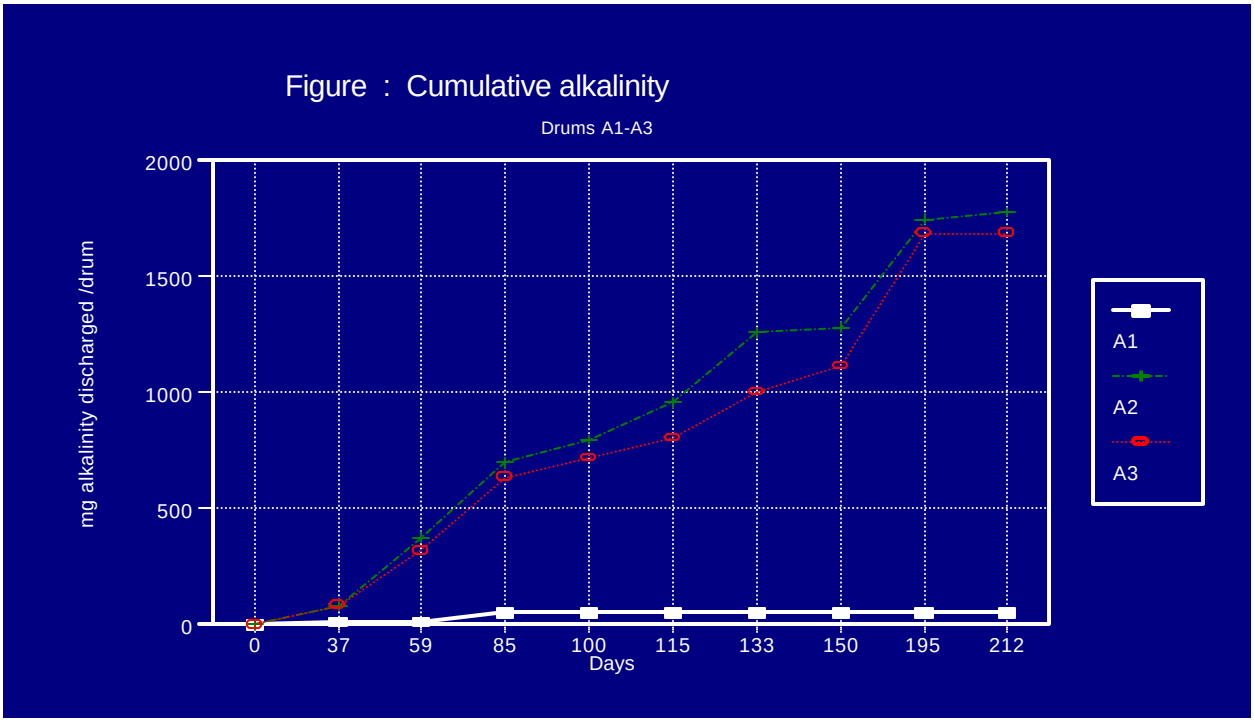


Figure : Cumulative alkalinity
Drums A1-A3
mg alkalinity discharged /drum
2000
1500
1000
500
0
0
37
59
85
100
115
133
150
195
212
Days
A1
A2
A3

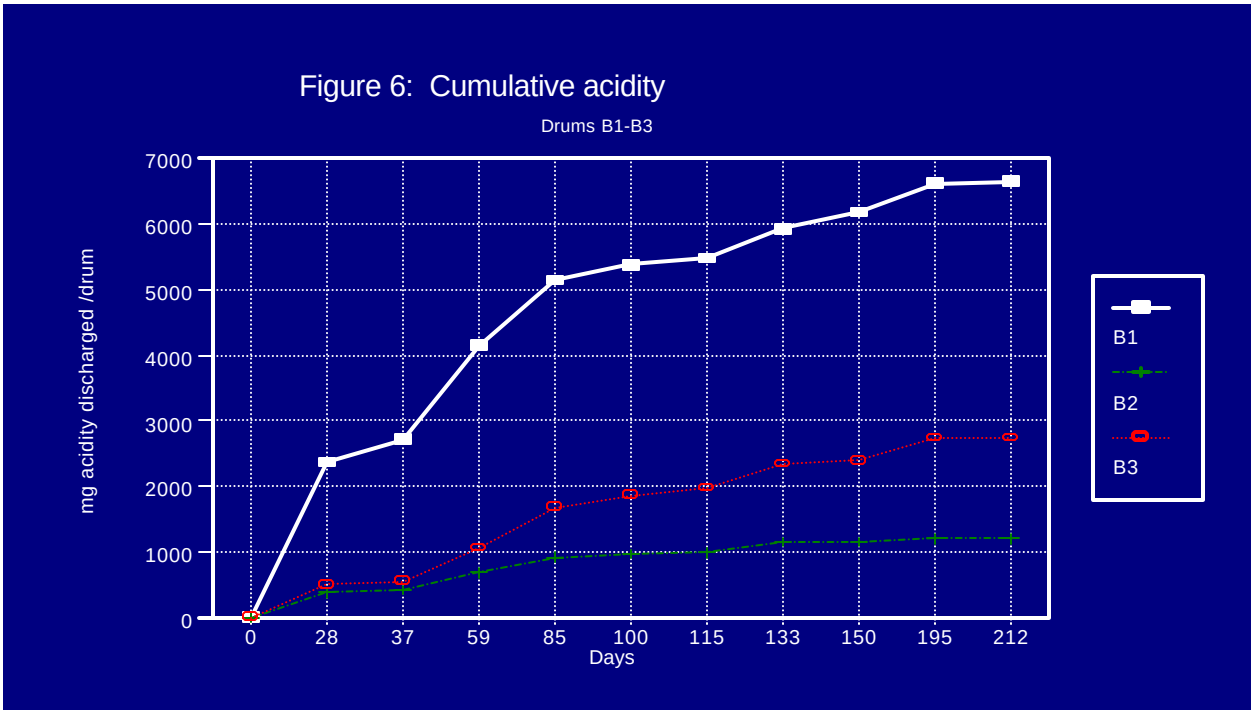


Figure 6: Cumulative acidity
Drums B1-B3
mg acidity discharged /drum
7000
6000
5000
4000
3000
2000
1000
0
0
28
37
59
85
100
115
133
150
195
212
Days
B1
B2
B3

Figure 7

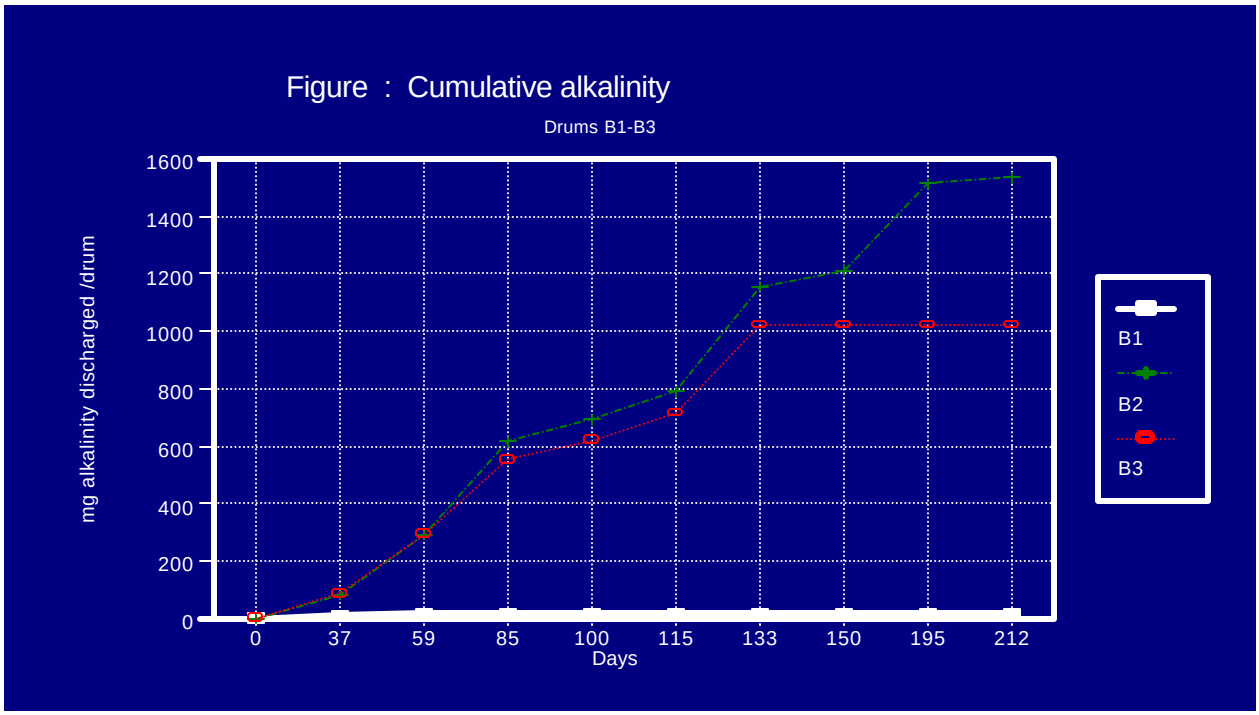


Figure : Cumulative alkalinity
Drums B1-B3
mg alkalinity discharged /drum
1600
1400
1200
1000
800
600
400
200
0
0
37
59
85
100
115
133
150
195
212
Days
B1
B2
B3

Figure 8

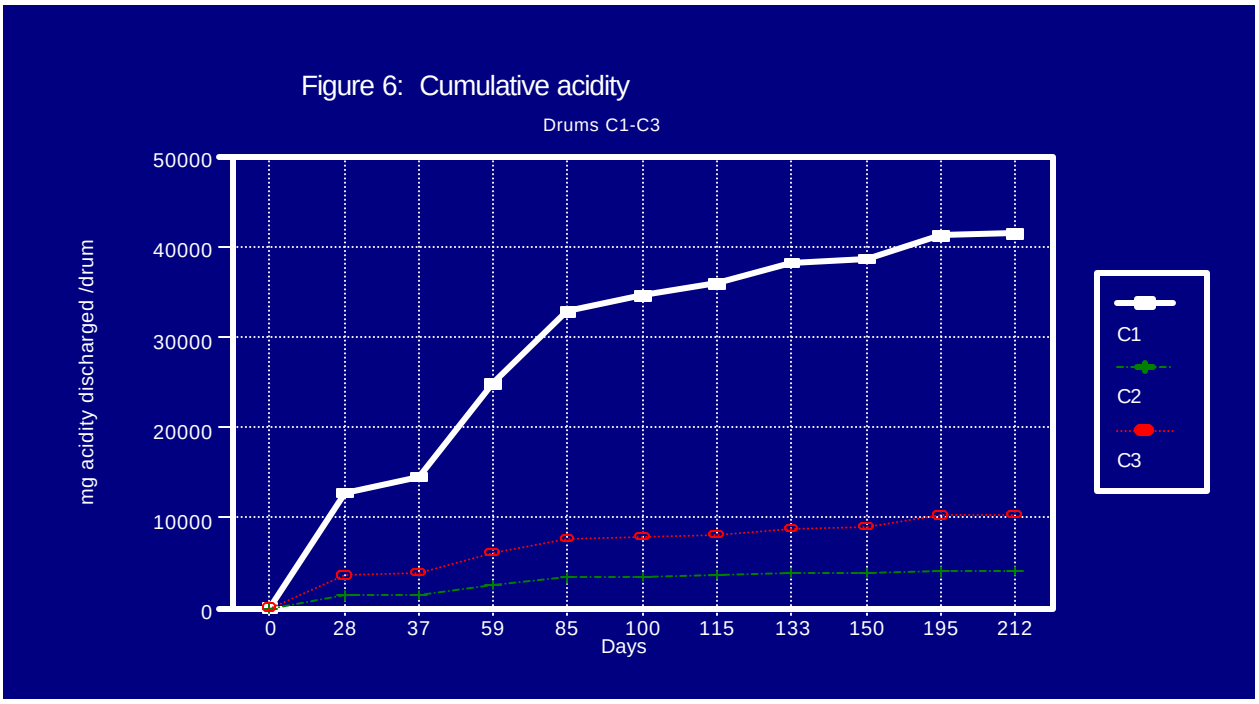


Figure 9

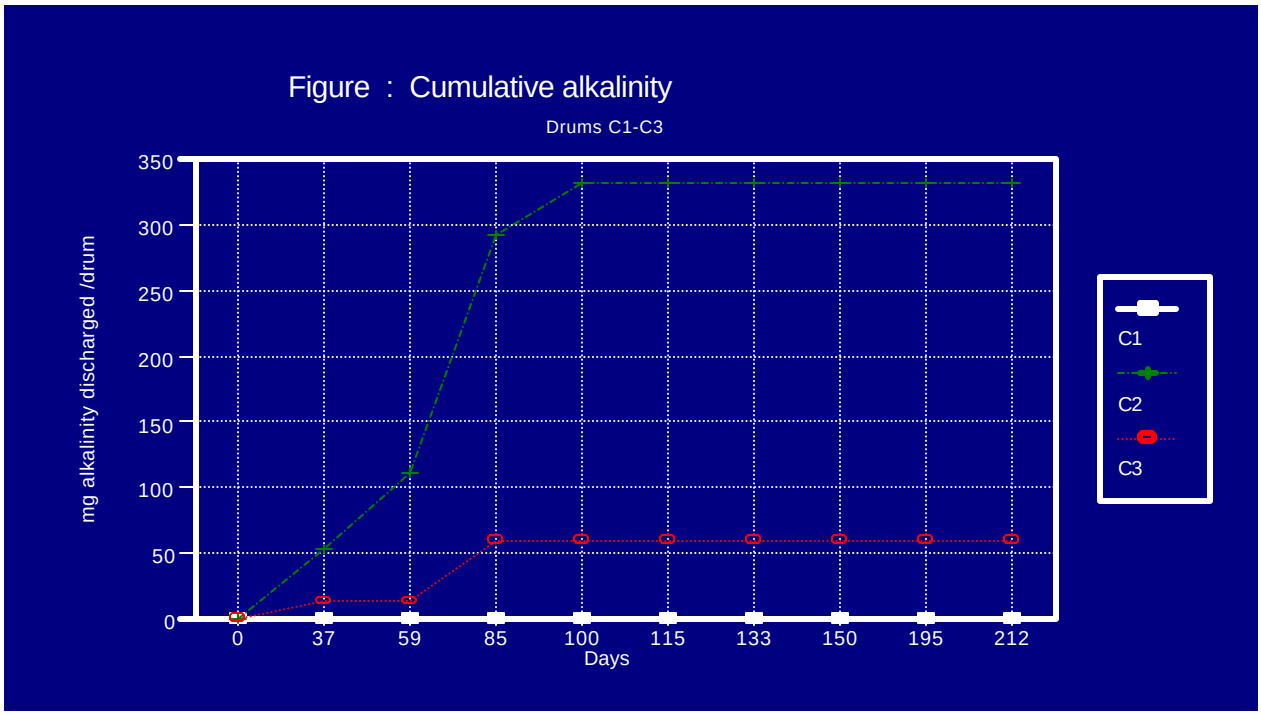


Figure 10

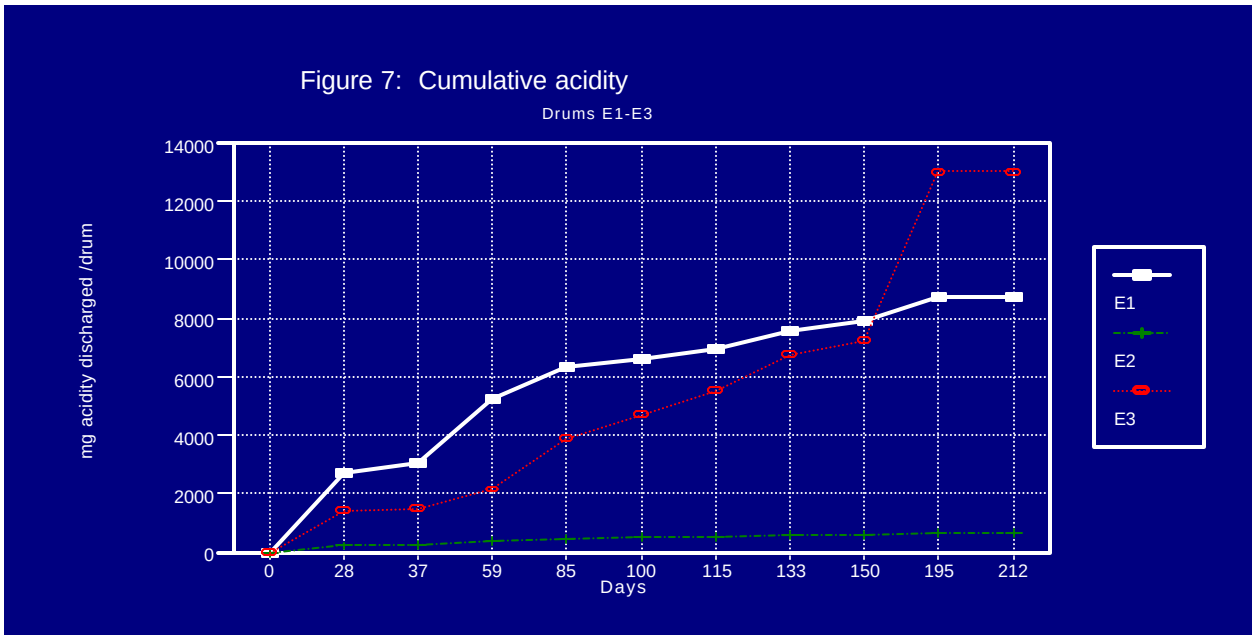


Figure 11

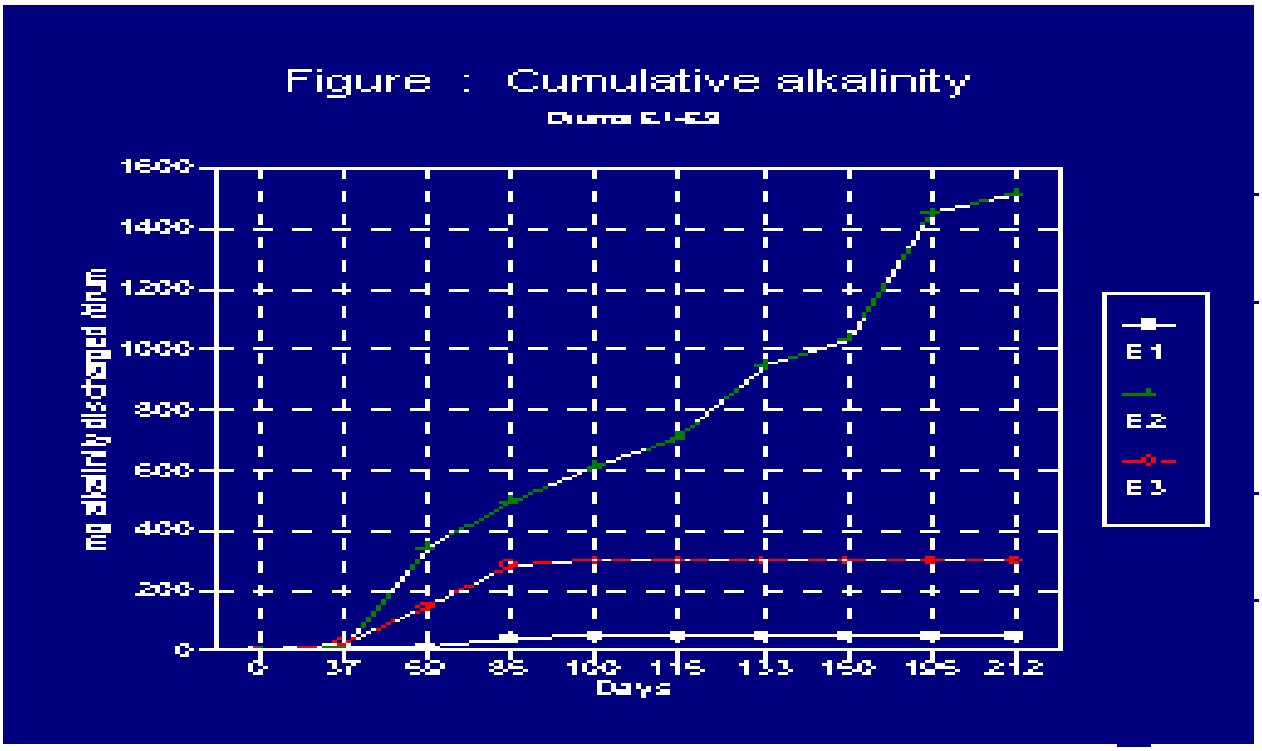


Figure 12

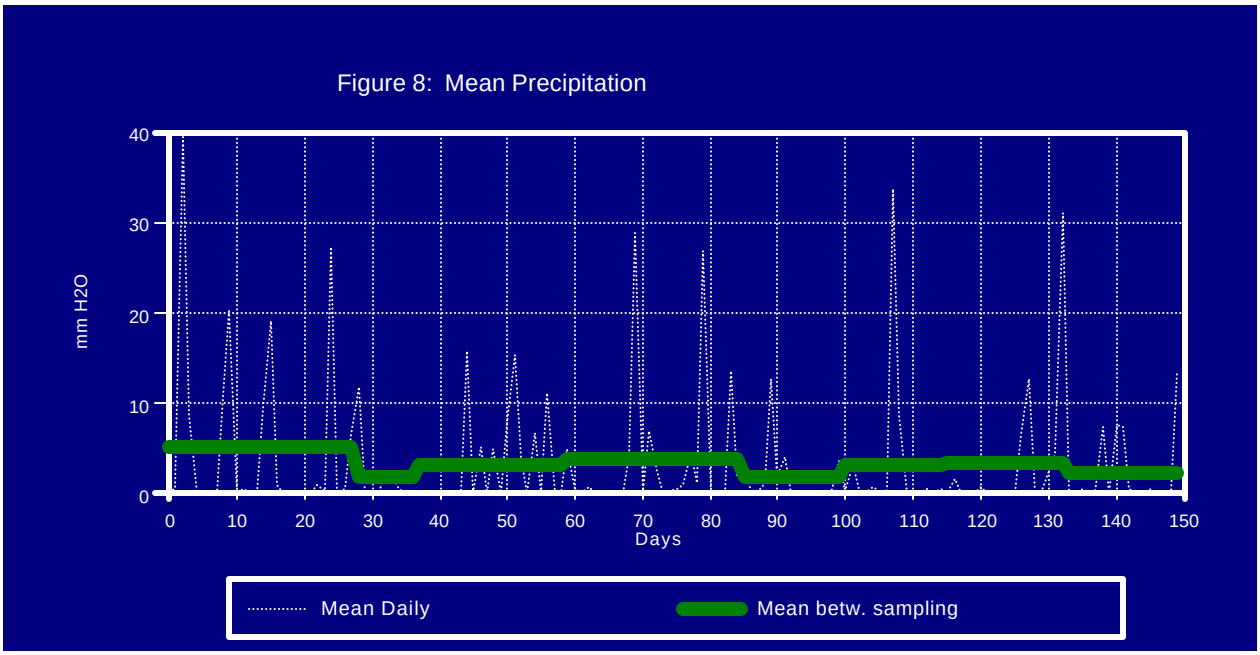
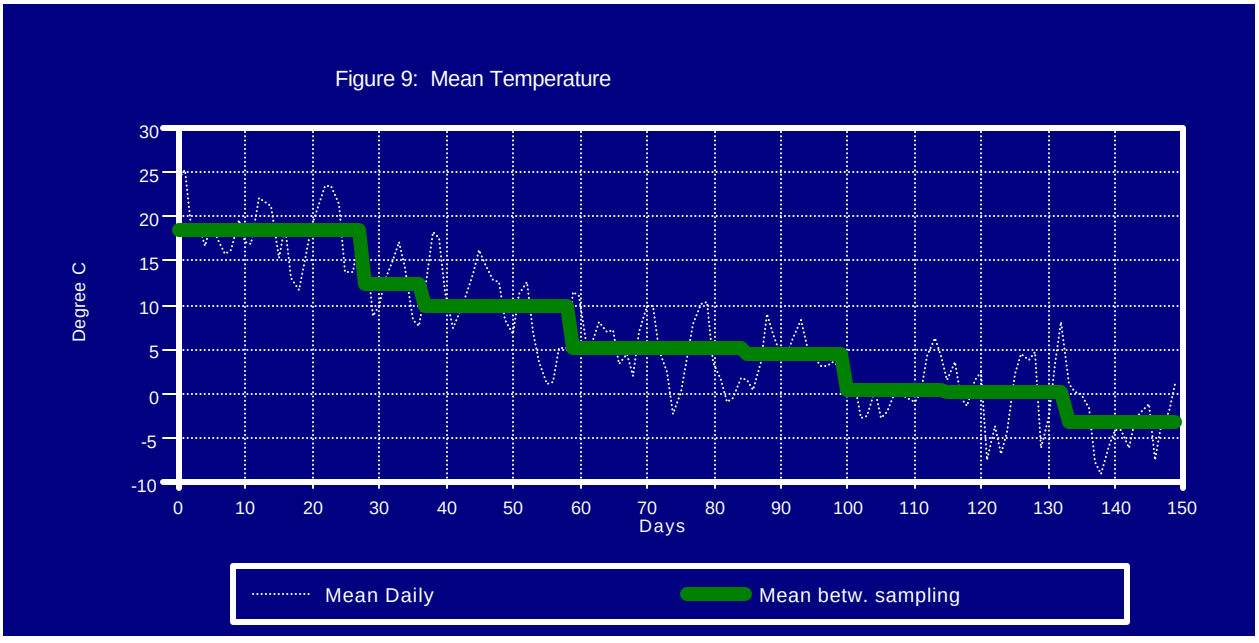


Figure 13



3.5 Conclusions

Monitoring results of the weathered rock in all drums indicate the onset of acid generation within 28 days. In general, weathered rocks generated more acidity than fresh rocks. Rates of acidity generation were much slower in the presence of NPR, regardless of rock type. Distribution of NPR throughout the rock column was much more effective in reducing acidity generation than confining the material to the top half of the drum. Acidity generation continued throughout the winter but was inhibited by low temperatures. The 17 drum set-up constructed in an outdoor facility at Boojum, is operating well, and is producing the anticipated results.

4.0 Scanning electron microscopy studies

Gibraltar Rock (background material) and rock samples from the drums (with or without phosphate rock), were examined by scanning electron microscopy at McMaster University. Two studies were made to test techniques for examination of rock surfaces in relation to morphology and chemical composition.

Surfaces of rocks were examined with the purpose of familiarization with surface morphology and for analysis (EDX) of surface materials to determine what if any secondary minerals are present and to relate the chemistry to surface morphology.

4.1 Methodology

Rock samples were chipped with a hammer. Pieces 1 to 4 cm in diameter were selected as these fit on stubs for SEM examination. Care was taken to minimise physical handling of the samples. The chips were handled with forceps. Immediately on sampling the chips were placed on sticky-tape within boxes to minimise physical disturbance and deposition of dust. Samples from the balcony were maintained at ambient temperature by chipping the rocks

outside and placing the samples in a cooler kept at ambient temperature. This will be critical for future studies employing cryo SEM where preservation of biofilms is required. Removal of samples from ambient temperature and humidity may result in drying out of the rock surfaces and/or deposition of condensation water which will complicate interpretation of observations since water droplets are preserved in this SEM method.

To collect samples from the barrels, a small flap was cut in the side of the barrel, one cut rock sample removed, chipped and replaced and the flap sealed back into place with silicone sealant.

Samples were mounted on stubs with a carbon-epoxy mixture (for effective electrical insulation) and coated with gold to a thickness of approximately 15 nm in a Polaron Cool sputter coater. Samples were examined in an ISI DS-130 scanning electron microscope. Samples were stored in a desiccator for future examination.

For analysis of surface materials, samples collected and mounted in the manner described above were coated with carbon in an Edwards evaporater carbon coater and subjected to EDX analysis with PGT System 4000 attached to the SEM. Image quality is much poorer with this set up but it enables electrons to reach the surface materials of the sample and cause emission of X-rays of wavelengths characteristic of the element. The X-ray spectra were collected and analyzed to determine the composition of original rock materials and secondary surface minerals. Direct quantification of elements or minerals is not possible except on perfectly flat samples because corrections for absorption require accurate determinations of X-ray path lengths (Blake, 1990). Fe:S ratios were used to determine whether iron sulphides are pyrite or other compounds (Fe_2S, FeS) which are undoubtedly secondary minerals. The ratio of the major peaks for what was clearly a pyrite crystal (C14) was <0.5 and in the study of Welton, ranged from 0.3 to 0.7. Deviations from this ratio indicate that other iron and/or sulphur compounds are present.

4.2 Results

4.2.1 Gibraltar rock

The Gibraltar rock material is believed to have secondary mineral coatings which have inhibited Cu oxidation in a leach heap. This material was examined by scanning electron microscopy to become familiar with the appearance and chemistry of such surface materials as determined by EDX analysis.

Gibraltar rock (Plate 1) exhibits a very open or porous structure. Flaky material is believed to be aluminum silicates (suggested by subsequent EDX studies). A variety of surface materials (e.g. the hypha-like bodies in Plate 1) are believed to be secondary minerals.

Examples of EDX spectra for Gibraltar rock are shown in Figures 14 and 15. The data for all spectra are summarised in Table 4. The EDX data (Table 4) indicate an abundance of Al, Fe, S and Si at most points examined. An example is shown in Figure 14. This is indicative of SiO_2, aluminum silicates and ferrous sulphides. The very high Fe:S ratio for GIBH indicates that ferric hydroxides predominate in this sample. This is undoubtedly a secondary mineral. The Fe:S ratios of GIBB, GIBD and GIBF (Figure 14) are 1.2, 1.3 and 1.0 respectively. Although the peak ratio cannot be directly equated to the molar ratio, they do give a clear indication of for example how reduced iron sulphides are and whether they are pyrite or FeS. Pyrite gives an Fe:S peak ratio of approximately 0.5. Ratios of 1 and above suggest that FeS may be present, undoubtedly another secondary mineral. The association of Na and K with Fe and S at these points suggests that jarosite ($AFe_3(SO_4)_2.(OH)_6$ where A may be Na^+, K^+ or NH_4^+), a secondary mineral, is present. Phosphate was present at five of the thirteen locations examined and may be a constituent of another secondary mineral. The only cations

always associated with P are Al and Fe. Either or both of these could form insoluble phosphates.

4.2.2 Drum waste rocks

Waste rock exposed to four years of weathering in the field and five months in a balcony drum was examined by SEM (Plates 2-4). Flaky materials, similar in appearance to those in Gibraltar rock were abundant. These are probably silica and aluminum silicates. Crystals, undoubtedly pyrite were also present. Some of these (e.g. Plate 2) had holes or pits at the apex which may be corrosion pits formed by oxidising bacteria (bacteria would not be readily identified with this method of sample preparation).

Low pyrite rocks exposed for only one winter prior to placement in the drums were examined both for surface morphology (gold coated) and for composition through EDX spectra (carbon coated). These samples were subject to leaching from phosphate rock placed higher in the drum. Examples are shown in Plates 3 and 4 and Figure 16 and 17. Secondary minerals were observed both on polished, freshly (5 months) exposed surfaces (Plate 3) and on surface previously exposed for one year in the field (Plate 4). EDX spectra failed to detect P on the sample examined. However, secondary minerals were certainly present. The carbon coated samples do not produce clear images. Flaky material subject to much charging (through absorbance of electrons) was mainly silicate as indicated by the EDX spectra. Fe, Al, S and Si were present in most samples as for Gibraltar rock but some examples of pure or almost pure SiO_2 were found (e.g. A34L and A34M in Table 4 and Figure 16). High calcium peaks (A34J) without other large peaks suggest the presence of $CaCO_3$ which may be a primary or secondary mineral. Very high Fe:S ratios were apparent for A34D and A34O (Figure 17) indicating the presence of iron oxides or carbonates both on exposed and polished surfaces. These are undoubtedly secondary minerals resulting from oxidation of pyrite in moist conditions.

4.2.3 Coal and coal precipitates

Samples of precipitates from laboratory columns of coal with were examined by SEM with EDX. These precipitates exhibiting a range of colours provide an opportunity to link physical appearance (colour) to chemistry (EDX spectra). Examples of spectra are shown in Figures 18 and 19. An orange precipitate (COALA) contains a large percentage of sulphur but also Al and Mg suggesting the presence of $MgSO_4$ and Al. The grey-green precipitate also contained much sulphur but also Fe, K and Mg. The high percentage of S in both precipitates indicates that elemental sulphur is present.

4.3 Summary

The two SEM sessions achieved the primary goal of testing methodology for examination of rock surface morphology and through EDX analysis to characterise primary and secondary minerals. Much experience was gained both in handling the sophisticated equipment and in interpreting images and data produced. Materials from only two drums in addition to Gibraltar rock and coal samples were examined but were sufficient to demonstrate that the McMaster facility can be used to examine rock surfaces. Secondary minerals were observed. In particular, the presence of P on Gibraltar rock bodes well for the development of phosphate-based, oxidation-inhibiting layers on waste-rock surfaces.

Table 4: Elemental composition of EDX scans

Sample	Scan	Description	Magn.	Element										
				Al	Ca	Cl	Fe	K	Mg	Na	P	S	Si	Fe:S
Low pyrite waste rock	A34A	Polished surface	2740				*					*	**	2
One winter weathering	A34B	"	2740	*			*					*	**	0.28
+ NPR leachate	A34C	"	2740	*			*		*			**	**	0.3
	A34D	"	2740	**	*				**			*	**	4.3
	A34E	"	2740				*					*	**	0.43
	A34F	"	2740		*		**					**	*	<0.5
	A34G	Polished surface-scan	102	*	*		*		*			**	**	<0.5
	A34H	"	102	*	*		*		*			**	**	<0.5
	A34I	Exposed surface	102	**	*				**			*	**	1.5
	A34J	"	102		**		*					*		7
	A34K	"	102				**					**		
	A34L	"	387										**	
	A34M	"	387										**	
	A34N	"	387				**					**	*	
	A34O	"	68	**	*		*		**			*	**	5.5
Gibraltar Rock	GIBA	Exposed surface	105	*			**	*	*		*	**	*	0.7
	GIBB	"	105	**			*	*		*		*	**	1.2
	GIBC	"	209	*			**				*	**	*	0.72
	GIBD	"	209	**	*		**	*	*		*	**	**	1.3
	GIBE	"	158	**	*		*				*	**	*	0.57
	GIBF	"	315	**	*		**	*		*	*	**	**	1
	GIBH	"	38				**					*		9.6
	GIBI	"	76	**			**					**	*	0.61
	GIBJ	"	76										**	
	GIBK	"	76	**									**	
	GIBL	"	76	*	*		*	*				*	**	0.25
	GIBM	"	76	**				*		*			**	
	GIBN	"	78	*	*		*					*	**	0.1
Pert pile coal	COALA	Orange precipitate	38	*					*			**	*	0
	COALB	Grey-green precipitate	38				*		*	*		**		0.1
	COALC	Grey-green precipitate	38				*		*	*		**		0.03
	COALD	Non-oxidised coal	504	*	*		*	*				*	**	0.27
	COALE	Non-oxidised coal-cryst	92	*	*		*					**	*	0.15
	COALF	Non-oxidised coal-next	92	*	*		*					**	*	0.16

** major peak
* minor peak

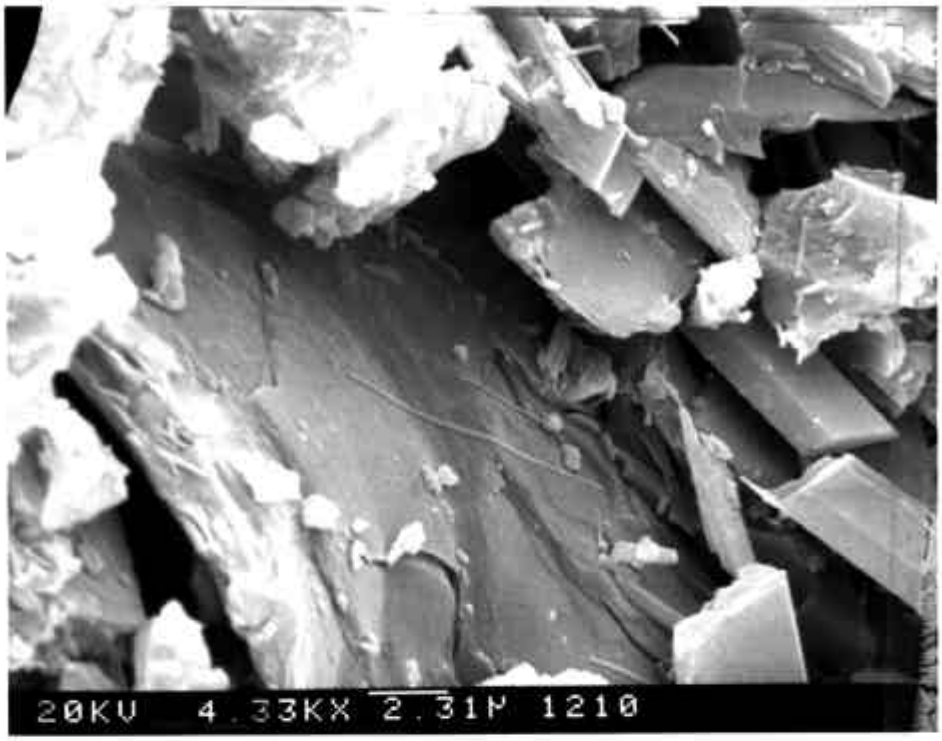


Plate 1: Gibraltar rock.

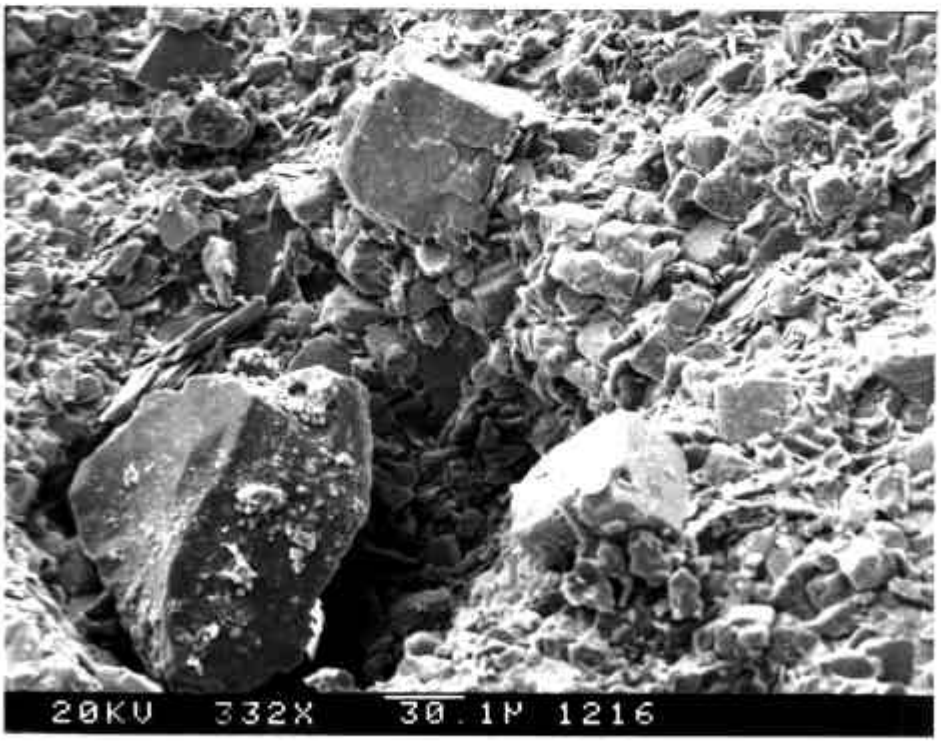


Plate 2: C-1, weathered waste rock - no NPR.
After 5 months in drum.

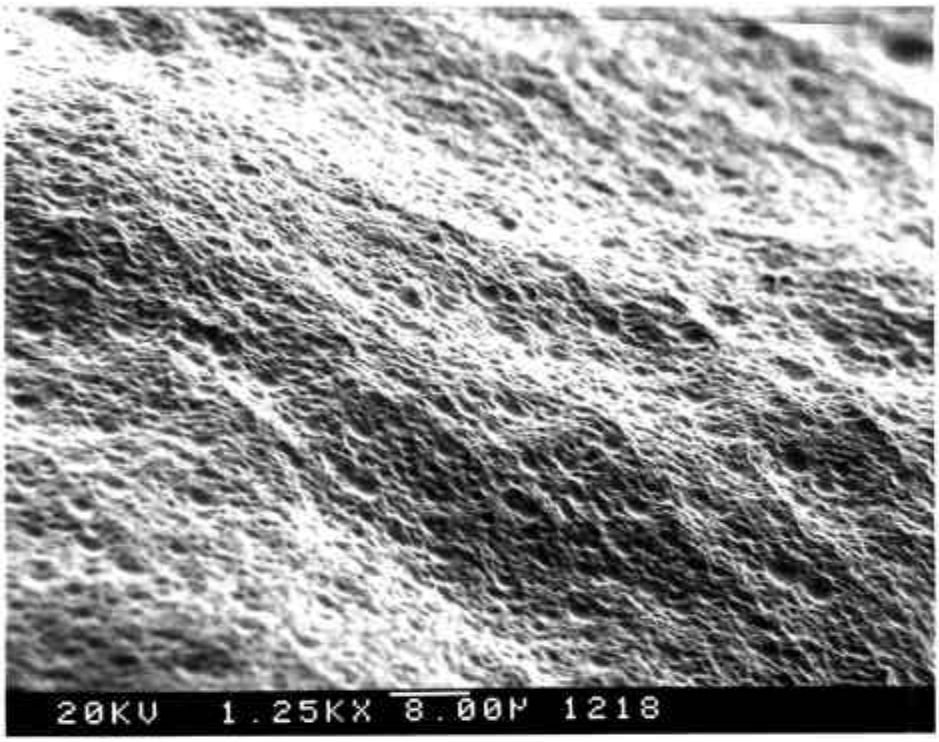


Plate 3: A-3, non-weathered, low pyrite rock - NPR not in direct contact. Polished surface. After 5 months in drum.

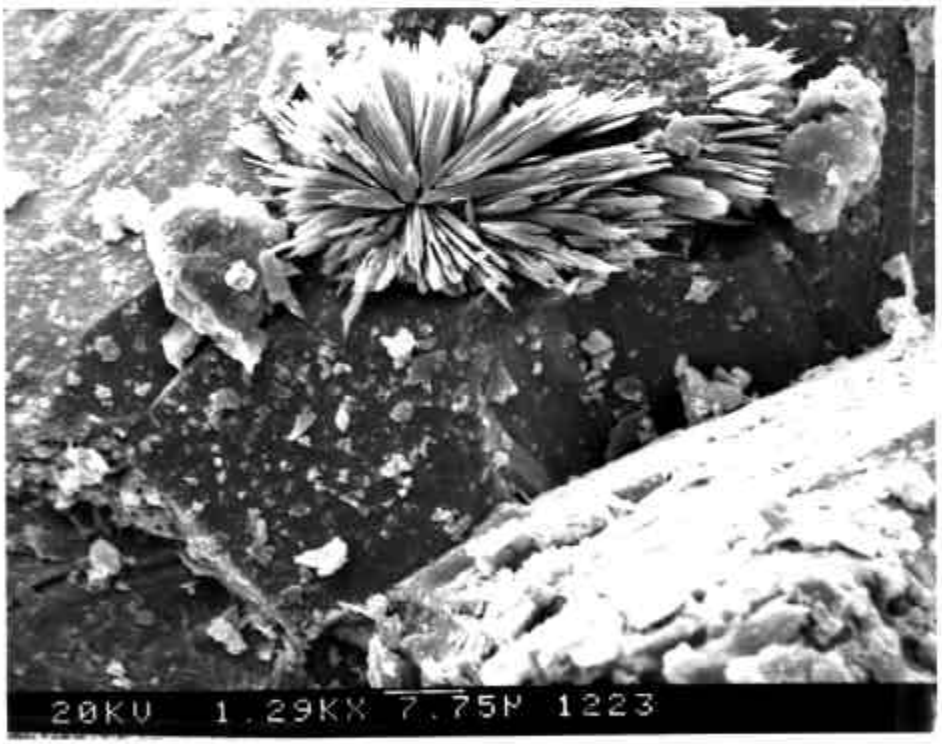


Plate 4: A-3, non weathered, low pyrite rock - NPR not in direct contact. Exposed surface. After 5 months in drum.

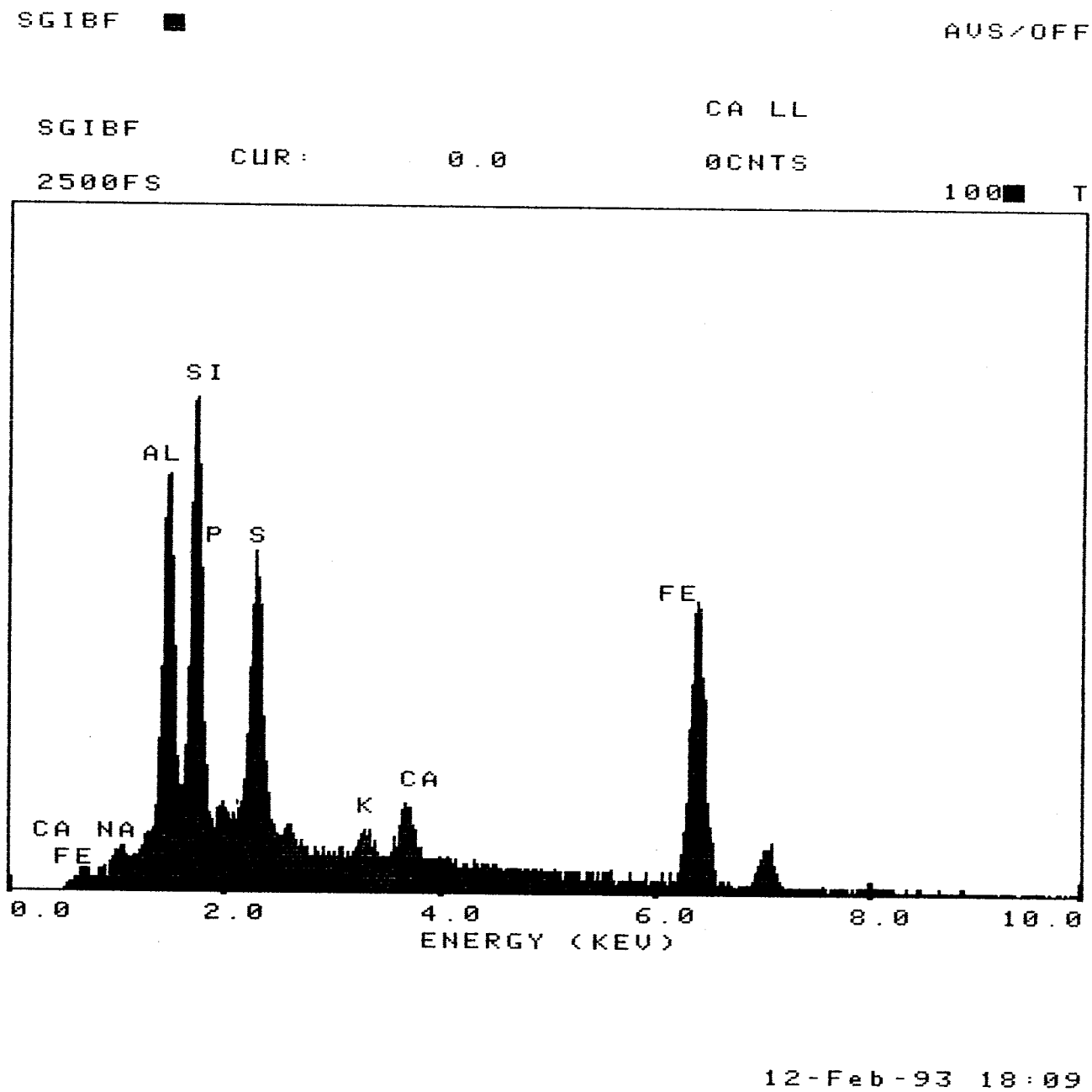


Figure 14: Gibraltar rock - EDX scan.

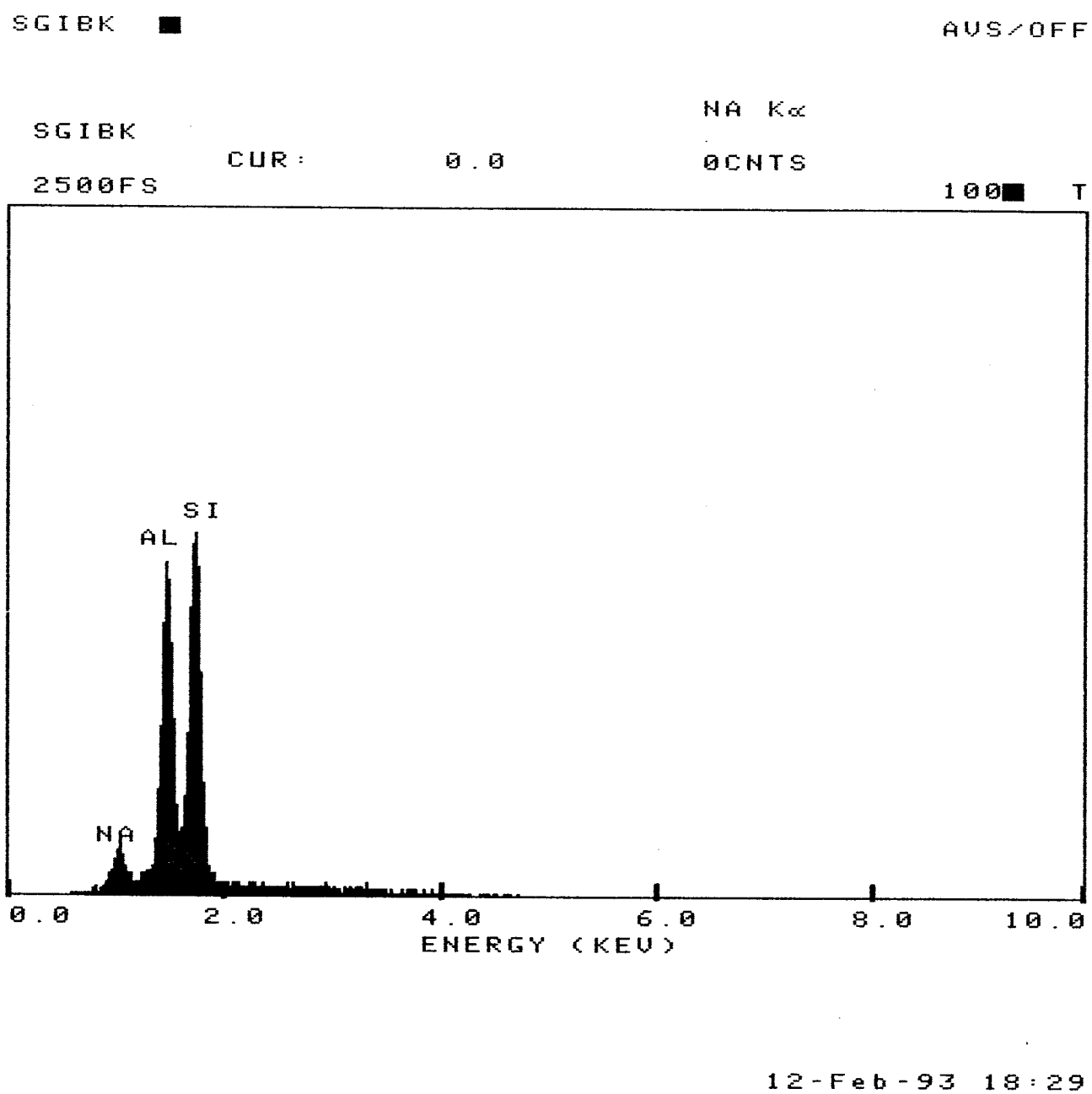


Figure 15: Gibraltar rock - EDX scan.

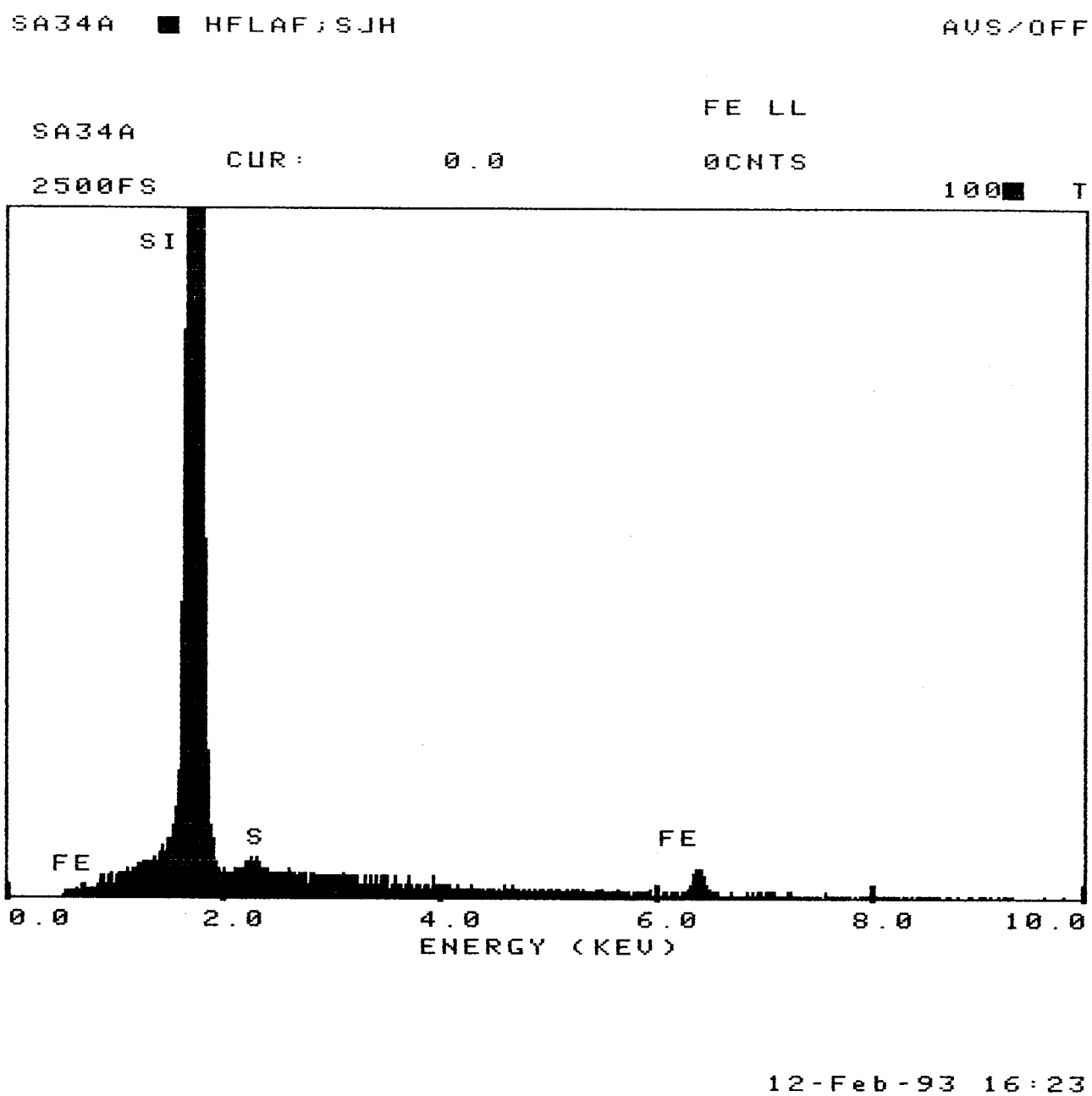


Figure 16: Non-weathered, low pyrite waste rock + NPR, not in direct contact. EDX - after 6 months in drum.

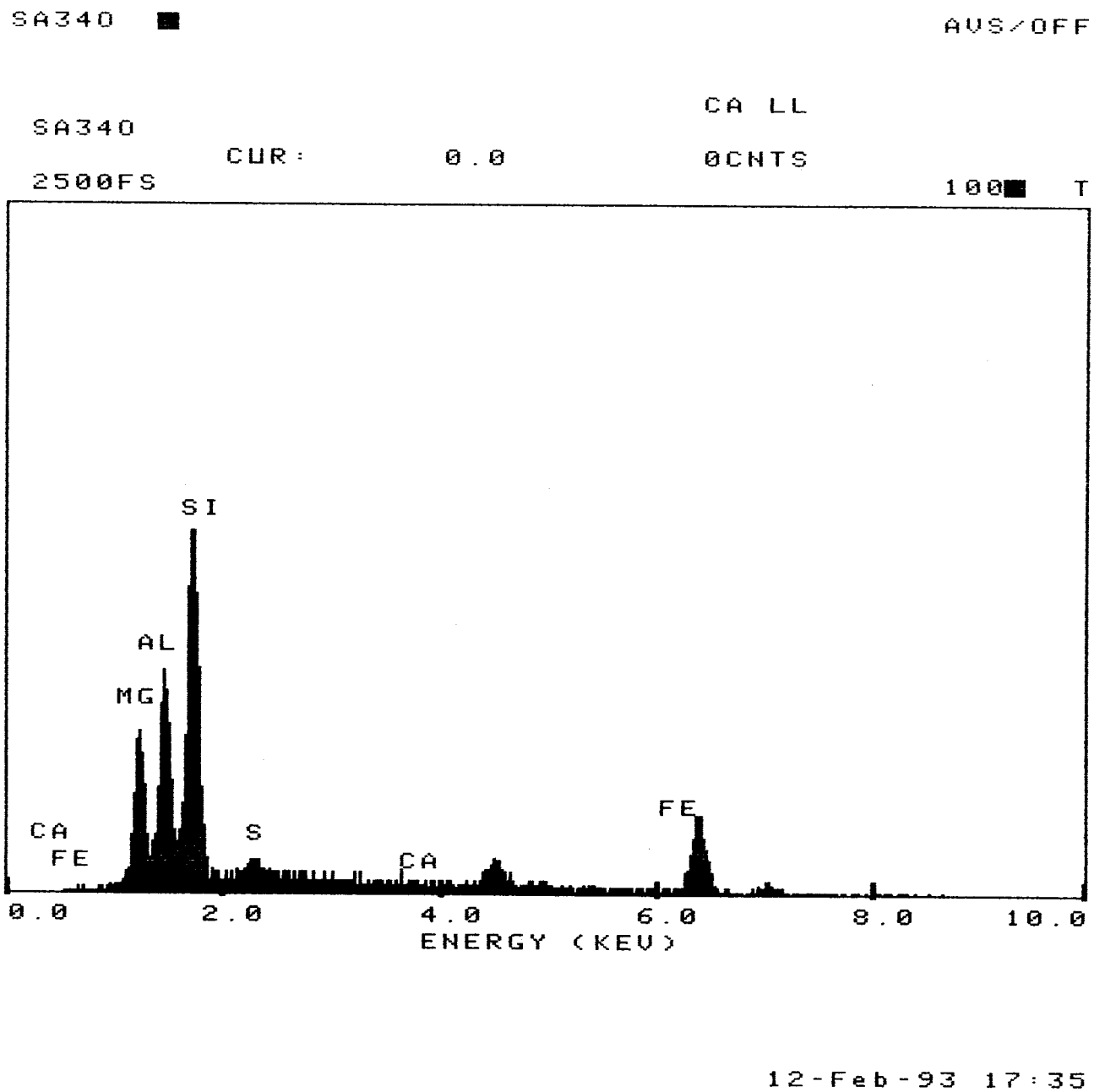


Figure 17: Non-weathered, low pyrite waste rock + NPR, not in direct contact. EDX - after 6 months in drum.

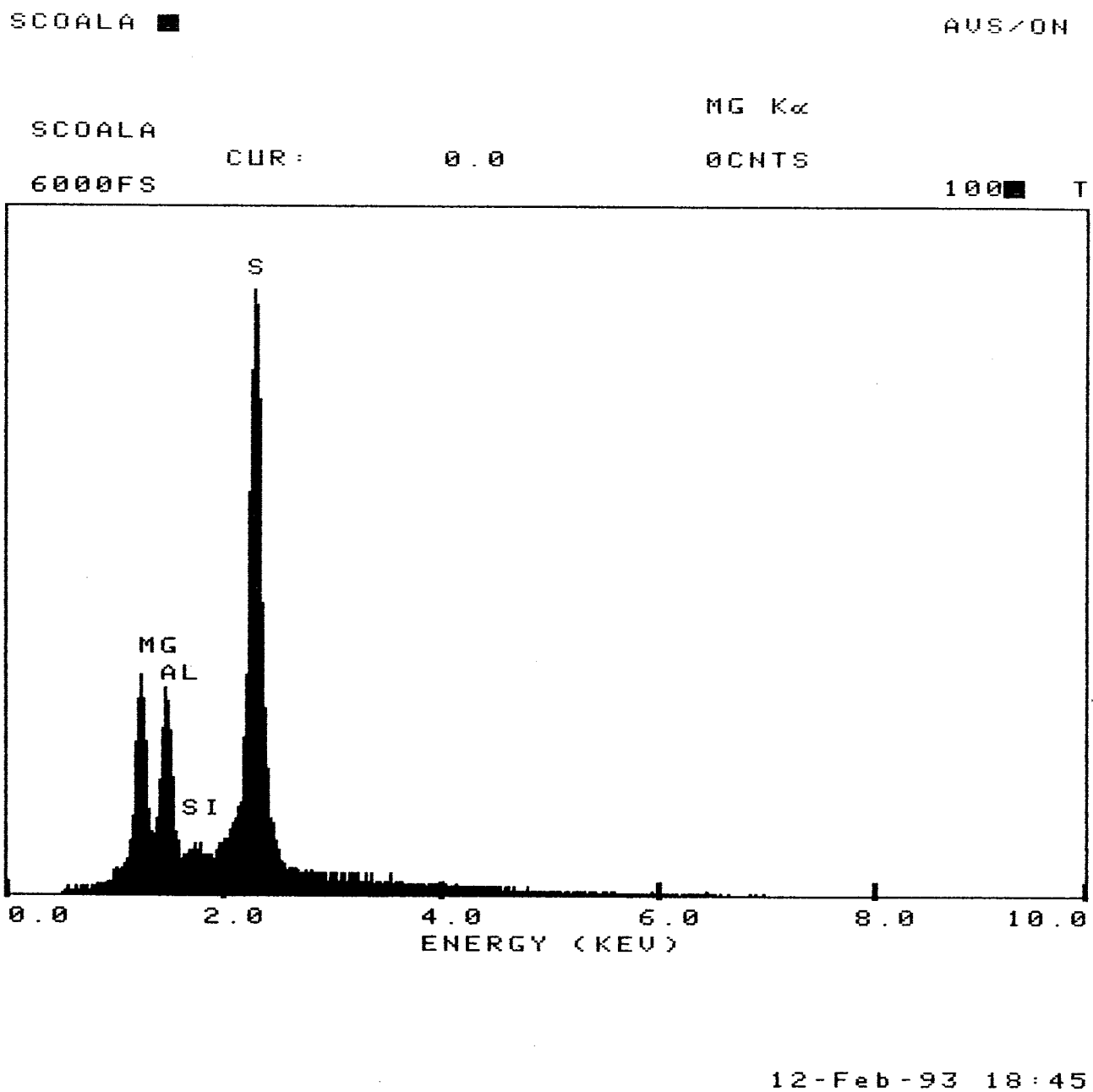


Figure 18: Pert pile coal, orange precipitate - EDX scan.

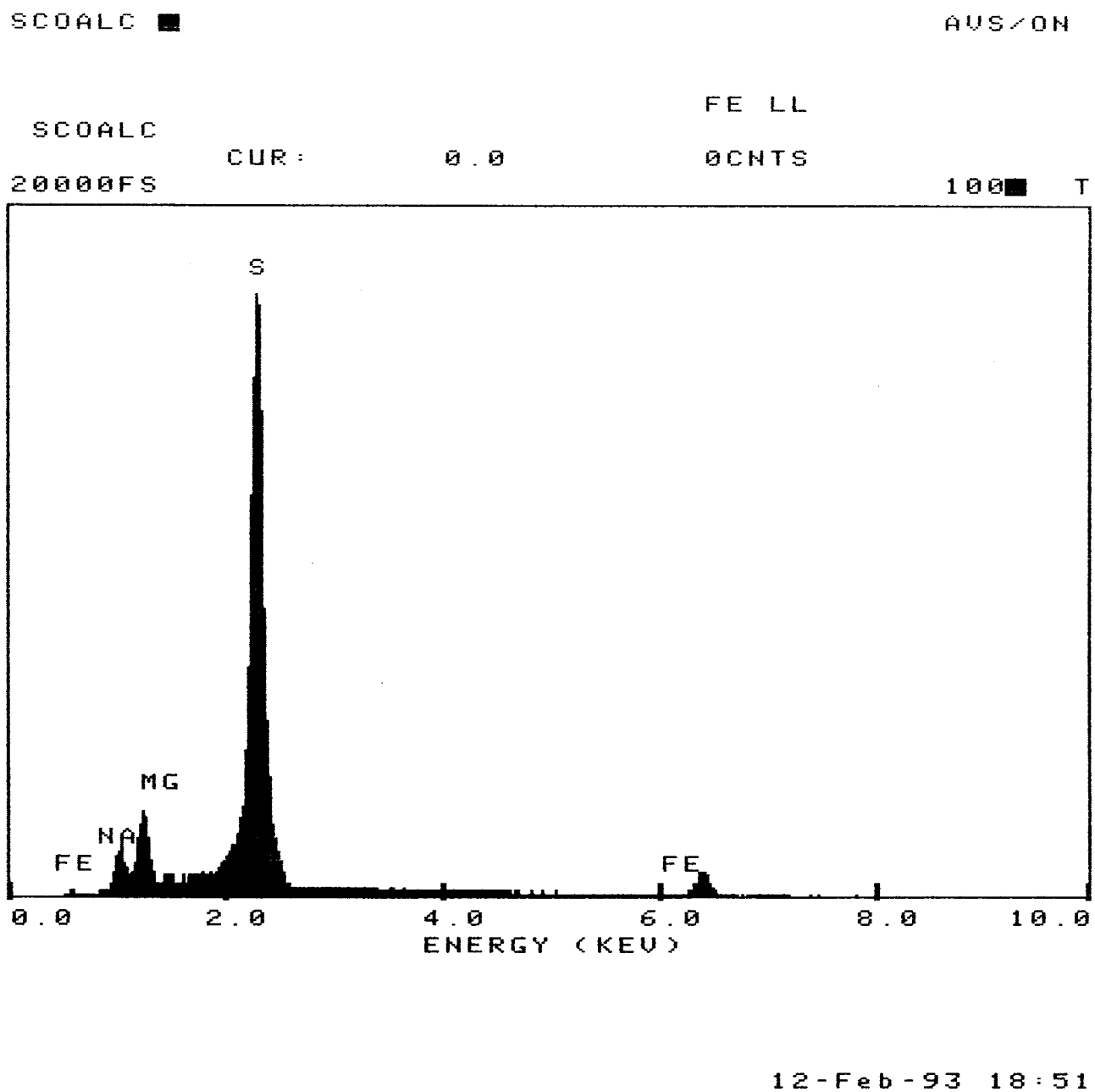


Figure 19: Pert pile coal, grey-green precipitate - EDX scan.

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USE OF NATURAL PHOSPHATE ROCK

AS

AN INHIBITOR OF ACID MINE DRAINGE

IN

C.B.D.C. COAL PERD PILE

APRIL 1993

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1. INTRODUCTION

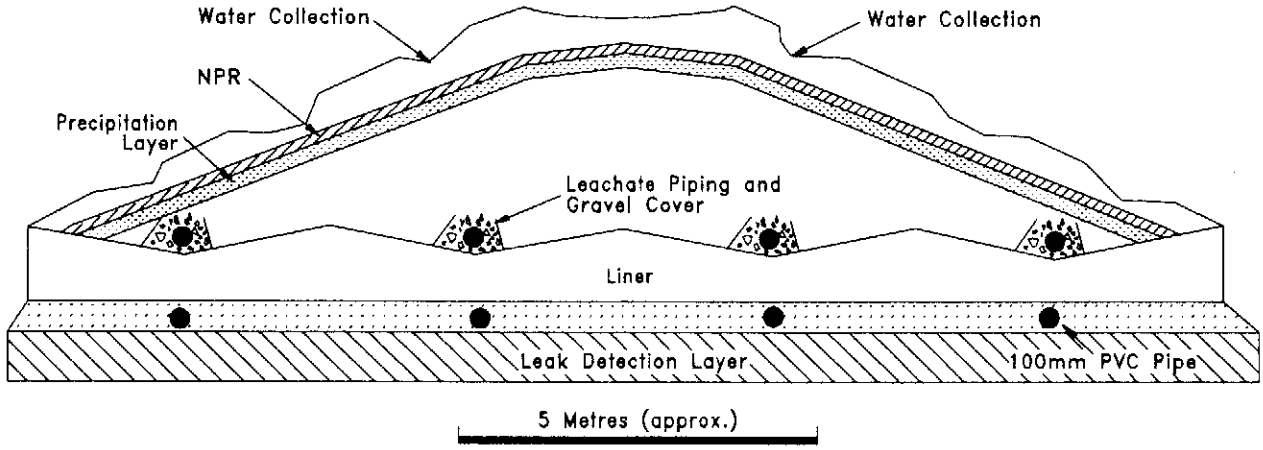
Coarse waste piles are significant sources of Acid Mine Drainage (AMD). Extensive research has been performed to find acceptable placement techniques and develop effective methods which would curtail acid generation from coal waste piles.

A study of placement techniques with integration of several neutralizing agents and bactericides, referred to as the PERD study, has been underway since 1991 at the Cape Breton Development Corporation. Test piles have been set up at the Victoria Junction Coal Preparation Plant in Sydney which are equipped with instruments to obtain the relevant data with respect to effectiveness of the methods and treatments. This work is carried out under contract to Nolan, Davis and Associates Ltd. project manager Ed Carey.

In 1992 Boojum Research Limited proposed adding a further pile to the PERD study using natural phosphate rock (NPR) as an inhibitor of AMD. The use of NPR as an ameliorating material for acid generating coal waste has been tested by several workers. This work has suggested that NPR was effective when mixed into coal waste (Ziemkiewicz et al. 1990) at 2 %. This application rate, however, renders the material non-economical and poses operational problems.
Boojum Research proposed to test the concept of preventing AMD in the PERD study by inserting a single layer of NPR into the coal pile as a final cover over the waste rock pile at the time of decommissioning. A second application of the material would be as thin layers on each lift of the coal pile.

Acid contacting the NPR will be neutralized and a hardpan (precipitation layer) will be formed which reduces permeability, due to the formation of precipitates. Furthermore, it can be expected that this reaction will take place directly on the coal surface, forming secondary minerals which might prevent further oxidation.

Under subcontract to Nolan, Davis & Associates, Boojum was requested to provide a conceptual design for the construction of the NPR PERD pile (Schematic 1). The NPR PERD pile was constructed using Long Harbour phosphate sand, remnants of a sedimentary rock from a fertilizer plant in Newfoundland. A layer about 5 cm thick was recommended, a thickness which was chosen without any experimentation prior to the construction of the test pile. The value was chosen based solely on economic considerations.



Schematic 1: Conceptual placement of NPR.

The results which will be obtained from measurements of the PERD pile at the VJ facility cannot be used to optimize the cover, nor will it be possible to determine if the NPR has indeed resulted producing a precipitation layer, as proposed. The PERD pile results will only give effluent quality data.

To develop the use of NPR as a cover or material to be integrated into the pile as an acid generation inhibitor in coarse coal waste, it was decided to design a laboratory experiment, which would address the needed information. In discussion with Ed Carey it was agreed that the objective of the work to be carried out under this contract by Boojum Research were to derive an experimental approach which would address all those variables inherent in the use of NPR as a cover, which could not be addressed with the field test pile.

In Section 2 of this report the experimental objectives are defined. In Section 3 the technical background required to determine the inhibitory effect of NPR on the coal waste and a critical review of the work on phosphate rock is presented. In Section 4 details of the proposed column experiment are presented, along with observations derived from two test columns and the estimates of the total amount of coal waste required for the experiment.

2. EXPERIMENT OBJECTIVES

Column experiments should provide the technical and scientific basis for developing the methods for coarse waste rock disposal which prevent, or significantly curtail, generation of acid from the coal waste dumps. It is expected that coarse coal waste interacting with NPR will achieve the following:

- affect water movement and, thereby possibly reduce the amount of contaminated water leaching from the dump;
- profoundly change the chemistry of the percolating water;
- develop a precipitate layer on coal surfaces reducing oxygen and water access to sulphides;
- possibly lead to bacterial consortium alteration resulting in AMD generation disturbances.

The focus of the column experiments is to address not only the functions above, but also to test the effects of variables such as:

1) thickness of an NPR layer,

2) type of NPR used.

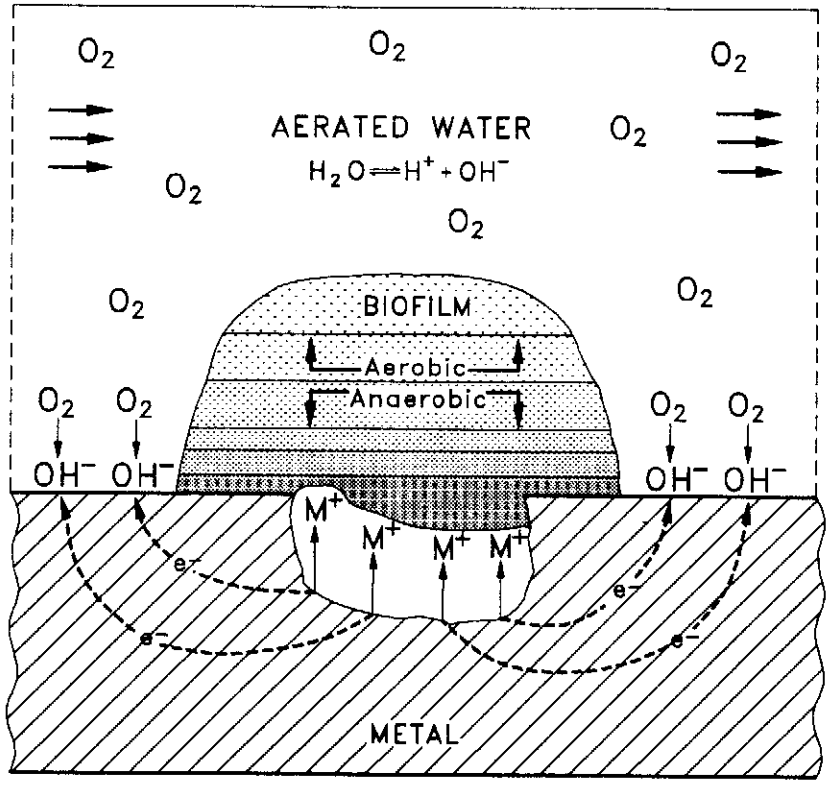
Long Harbour phosphate sand is unprocessed material. Texasgulf produces several fertilizers for acidic soils with different concentrations of phosphate and different grain sizes (a large- grained product of NPR containing about 19 % phosphate (P_2O_5) and a processed, powdered product labelled Code 30 containing a minimum 30 % (P_2O_5).

It can be expected that compacted piles are better in principle than non-compacted piles, because the significant content of mudstone and clays in the coarse waste will retard the onset of AMD generation. The close contact of NPR material to acid-generating coal is essential. Therefore, finer-grained material, which more easily penetrates the compacted pile, should be tested, even though it is more expensive.

3. TECHNICAL BACKGROUND

Oxidation of sulphur-rich coal waste, which may lead to AMD generation, is enhanced by bacteria. The process may be simply described as sulphide oxidation to sulphate in the presence of oxidizing bacteria such as *Thiobacillus*.

This bacterially-mediated oxidation occurs in very close proximity to the sulphides. Bacteria live in a biofilm which is micron-thin. Oxygen must diffuse into that biofilm and this can be the reaction-controlling factor. Preventive methods, therefore, have to reach the level of the corrosion pit on the surface of the pyrite. Schematic 2 shows a cross-section of a biofilm. The column experiment will provide material which can be destructively analyzed at the end of an experiment. It is proposed to carry out an SEM investigation of the biofilm on pyrite on selected coal pieces.



Schematic 2: Cross-section of biofilm (after Little et al. 1990).

Conventional SEM employs the critical point drying method. The McMaster University electron microscope facility in Hamilton, Ontario is equipped for cryo-SEM. Instead of drying, the sample is very rapidly frozen in semi-solid nitrogen (-220^{o}C). This procedure preserves the hydrated materials without the distortions caused by drying (Campbell and Porter, 1982; Read et al, 1983; Fyson et al, 1988). In other words, three-dimensional relationships between rock-surface, biofilms and precipitates are preserved.

Water may obscure the location of bacteria. This can be overcome, either by fracturing the biofilm on the microscope stage and by etching (localised heating) of the sample to progressively lift the water and reveal previously buried material. Freezing will also preserve the chemistry of the surface materials (Blake, 1990). Comparison to reference solutions in conjunction with EDX analysis will help identify the compounds in the aqueous layer, e.g. suspended solids and solutes. EDX analysis can also help identify precipitates, and in conjunction with direct observation of crystal characteristics, the chemistry of surface materials. Thiobacilli will be isolated and enumerated. Other bacteria present will also be characterised.

3.1 The Use of Phosphate Rock in AMD Material, A Critical Review

Preventive measures for the inhibition of acid generation have to consist of two key components. First, the oxygen which is required for the microbial oxidation of the pyritic material must be consumed. Second, the acid which has been produced on the surface of the pyrite has to be neutralized. This can best be achieved in the immediate vicinity of the pyrite where the acid is generated.

Phosphatic material has been tested mainly with coal refuse as a neutralizing agent. The work which has been published to date is reviewed with respect to the preventive nature of the material.

Reclamation Research Unit-Montana State University, 1990. E. Spotts, D.J. Dollhopf Evaluation of Phosphate Sources for Control of AMD in Coal Overburden. pp 1-69.

"... concentration of free Fe^{+3} and its ability to oxidize FeS_2 is dramatically reduced by the addition of a source of phosphate ions (PO_4^{-3}). Phosphate is effective in this regard because it can precipitate the Fe^{+3} ion in a relatively insoluble form as a $FePO_4$. It can also precipitate Fe^{+2} as $Fe_3(PO_4)_2$ rendering it unavailable for oxidation to Fe^{+3}, either by bacteria or oxygen. In addition the iron phosphates can precipitate on the surface of FeS_2 crystals, further limiting FeS_2 reactivity" (pg. 17).

This statement of the authors indicates the preventive and neutralizing usage of phosphate. However no evidence is given that oxidation of the phosphate precipitate may not take place. The literature has to be evaluated from the microbial point of view and the oxidation of reduced iron precipitates has to be evaluated chemically, to confirm or refute the statement made.

"... apatite was more effective in controlling acid production than either sodium lauryl sulfate or limestone. In addition, the rates of apatite required to effectively control acid production were approximately five times less by weight than the amount of limestone needed, indicating that the use of apatite for the control of AMD may be considerably less expensive than a similar use of limestone, assuming both sources are readily available" (pg. 17&18).

Comparing apatite to limestone or the sodium lauryl sulfate as agents controlling acid generation is inappropriate, based on the effects which can be expected from these different products. Limestone can only neutralize acid which is already generated. Sodium lauryl sulfate is a bactericide (surfactant) which would kill the oxidizing bacteria, resulting in a slower rate of acid generation. Apatite has two functions, neutralization due to the carbonate component and formation of iron precipitates on the surface of the rock.

The rates of application are stated to be five times less by weight than limestone. This is partly a function of the density of the material. The density of limestone (2.6 to 2.7, Handbook of Physics and Chemistry) is higher than that of apatite which is 1.6 (Texasgulf-specification of Code 30). Limestone will only neutralize the acid generated and will not inhibit acid generation. Therefore in order to assess the application rates of limestone and phosphate rock (apatite), the following considerations have to be made.

The application rate for limestone is a function of the total acidity which has been generated from the AMD material and also of the acid generating potential of the material i.e. the total acid mine drainage which could be generated from the material. For phosphate rock, the application rate will depend on the acid already generated in the material and the metal concentrations, particularly iron, available to form precipitates. The effectiveness of the inhibition will largely be a function of the contact of the solubility products of apatite and its formation of secondary minerals on the pyrite surface.

The statement on the economics is not substantiated, since it does not consider a $ value for reduction (the inhibition of the acid generated). The shipping costs, have to be evaluated with respect of costs per tonne of alkalinity which can be generated from the material. Since phosphate rock is denser, the economics of shipping should be evaluated based on the amount of alkalinity per tonne shipped and the amount of iron precipitation material per tonne shipped, not taking into account either bulk cost of medium or transport.

"... the insolubility of apatite above pH of approximately 4.5 insures that PO_4^{3-} ions will be available as an *in situ*, point source control of AMD until the pH drops to this value. At this point the dissolution of apatite renders PO_4^{3-} ions available for the precipitation of iron. At this point, the dissolution of hydroxy apatite also liberates hydroxyl groups into solution, providing a source for H^+ neutralization" (pg.18).

The solubility of apatite depends on the pH of the solution and in principle it is not insoluble. At pH 7 the following reaction will take place:

$$Ca_3(PO_4)_2 \rightarrow 3Ca^{+2} + 2PO_4^{-3}$$

and at pH 4.5 the following reactions will occur:

$$Ca_3(PO_4)_2 + 2H^+ \rightarrow 3Ca^{+2} + 2HPO_4^{-2}$$

$$Ca_3(PO_4)_2 + 4H^+ \rightarrow 3Ca^{+2} + 2H_2PO_4^-$$

The rate at which these reactions will take place is also different, i.e. at higher pH lower reaction rates and at lower pH higher dissolution rates can be expected. The effectiveness of apatite as an inhibitor of acid generation, lays in the production of precipitates with iron below pH 4.5 and therefore in the contact with the acid generating source, i.e. the pyritic surface where pH is always low.

Providing the correct mixing conditions is one of the main reasons for the proposed test plots. There is a wide range in particle size of the uranium tailings, base metal tailings and the waste rock. The application methods will be those used in general tailings reclamation, where INCO agriculture has extensive expertise.

"The performance of the Texas Gulf ore at 3 % application rate was not markedly better than The Stauffer sludge at 5 % rate of application. Although it achieved the most significant reductions in acidity, Stauffer sludge at 5 % was just as effective at reducing Fe levels and both initial (cycle 1) and cumulative S concentrations. Since it was not the objective of this study to evaluate the feasibility of the use of the Texas Gulf ore as an amendment in the western United States, this issue will not be addressed. However, the performance of the Stauffer sludge relative to this source is encouraging, especially in light of the results of previous research (Renton 1988, The use of Phosphate Materials as Ameliorants for AMD. Mine Drainage and Surface Reclamation, Conference in Pittsburgh, Pensylvania, pp 67-75), which had determined the Texas Gulf ore to be a very effective source of phosphate at controlling acid production relative to other sources tested" (pg. 58).

Other sources of phosphate were: Cominco ore (apatite mined from the Permian Phosphoria Formation near Garrison Montana), Cominco waste (byproduct of the washing of crushed ore - Garrison), Stauffer ore (apatite mined from Permian Phosphoria Formation in southeastern Idaho), Stauffer sludge (dried slurry material being byproduct of elemental phosphate production), Triple Super Phosphate (commercially available calcium phosphate fertilizer) and Texasgulf (processed apatite rock).

It is of more than passing interest to recognize that different materials in this work produced different results. This is likely due to the fact that the solubility changes with respect to mineralization and processing of the material. The reaction kinetics are related to surface area (different grinds are being tested presently, to design the test plots) and processing. A calcined phosphate rock reacts much faster than non-calcined product.

P.F. Ziemkiewicz et al., 1990. Advances in the prediction and control of AMD. IN: Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Vol. 1, Charleston W. Virginia, 1990, pp 93-101

"It should be also stressed that phosphate is not being used as a neutralizing agent. Application of phosphate to mine refuse rock surfaces creates a physical and chemical environment which prevents the formation of acid. Iron ions from pyrite grains are prevented from reacting with water and oxygen by participating in a faster reaction with the phosphate anions. Subsequent precipitation of insoluble iron phosphate salts may further inhibit availability of reacting pyrite sites. Neutralizing agents such as limestone, on the other hand, permit the oxidation of pyrite to occur and than react with the products. This is why massive amounts of neutralizing agents are required to control AMD. It is unlikely that addition of low ratios of phosphate to already oxidized rock will have much beneficial effect" (pg.94).

This point of the author stresses the difference between limestone and phosphate rock as an approach to the preventive advantages and also stresses that phosphate should not be considered only as neutralizing material.

"... The effectiveness of rock phosphate in controlling AMD production has been demonstrated in both laboratory and small scale field trials" (pg. 96).

The full scale application has to be tested. To our knowledge the full scale applications were not carried out due to economic considerations. However, to date, it has not been possible to ascertain details which lead to this decision.

Tech-Talk. Review of latest 'new technology' publications. Canadian Mining Journal, February 1993, pp 21-23.

It is stated in the review of the book by R.K.Singhai, Environmental issues and management of waste in energy and mineral production. A.A. Balkema Publishers, Brookfield, Vt. 1487 pp. that: "Scientists at the University of Kentucky, for example, report here on a permanent, cost effective way to prevent pyrite - one of the main culprits in AMD in coal wastes -from oxidizing. The technique involves coating pyrite with a relatively inert ferric phosphate. "The coatings shut off electron transfer between pyrite and oxidizers necessary for oxidation", Says Bill Evangelou and Ziao Huang of the university.

This statement, by a preeminent acid mine drainage chemist confirms the proposed inhibition role of phosphate rock, in the application to be developed.

A. F. Meek Jr., (1991). Assessment of acid prevention techniques employed at the Island Creek Mining. IN: Twelfth Annual West Virginia Surface Mine Drainage Task Force Symposium, April 1991, pp 1-9.

"As shown, the most cost effective acid preventive technique employed at the Upshur Complex was selective handling and placement with phosphate/apatite admixed technique. In the conclusion, it can be said that none of the techniques attempted were entirely successful in the complete elimination of AMD" (pg 7).

The phosphate was compared with: selective placement, selective placement with PCV liner, selective placement with lime, and proved to be the most economically viable. The pilot scale experiment results are based on 6 years of observation. It is not unreasonable to expect, that complete inhibition was not achieved, since the optimal mixing and type of apatite would have to be determined, prior to the field tests.

Paul F. Ziemkiewicz, Jeffrey G. Skousen, 1992. Prevention of Acid Mine Drainage by Alkaline Addition. IN: Proceedings of the 13th Annual W.Virginia Surface Mine Drainage Task Force Symposium, 10 pp.

" The results indicate that at least under laboratory conditions, a ratio of neutralization potential to maximum potential acidity (NP/MPA) of 0.35 or greater resulted in neutral to alkaline leachate" (pg.1).

"Supporting the latter contention is the NP/MPA ratio at which AMD is controlled in laboratory tests. For kiln dust and FBC ash the ratio was 0.35 or greater. Phosphate was lower in two cases, generating neutral drainage (e.g. greater than 6.0) with ratios of 0.18 (samples 8078 and 8096). The NP of the rock phosphate **used in this study was only 0.14** (measured NP expressed in percent calcium carbonate equivalent for each of the amendments were: kiln dust 99%, FBC ash 26%, phosphate 14% - pg. 7), suggesting that at least some of its effect on acidity reduction may stem from precipitation of iron phosphate. Except for these two phosphate treatments, every sample which had an NP/MPA ratio of 0.35 or greater generated neutral drainage" (pg. 7).

In this work the phosphate amendment is at a disadvantage because of the experimental design. The experiment compares materials which are assumed to mitigate AMD in different ways, yet draws conclusions based solely on neutralisation potential (NP).

AMD neutralization by kiln dust would be more effective since it is readily soluble and contains 99% equivalent of calcium carbonate. The authors have already stated in 1990, that phosphate use for neutralization would unlikely be beneficial, as it should not be considered as a limestone substitute or neutralization agent alone.

"Other alkaline materials has higher NP's than calcite. Quicklime, kiln dust, and hydrated lime all have higher activities than calcite, though it is not clear that the kinetics of pyrite oxidation favour readily soluble sources of alkalinity" (pg. 3).

The kinetics of interaction between phosphate and refuse is quite different from that of the other amendments used in the experiment.

"To be an efficient process, the acid-forming and alkaline rock must be thoroughly mixed. This largely becomes a materials handling issue" (pg. 4).

In the tailings pile, acid is mostly generated in the vadose zone. It is not realistic to expect to mix the phosphate rock into the entire tailings deposit to achieve a mixture which would facilitate contact between the pyrite surface and the apatite. The proposed tailings cover applications integrate the material only in the upper surface of the tailings pile and at the same time promote the growth of oxygen consuming bacteria.

"The data, **excluding** the phosphate data, were used to develop a simple curvilinear regression model to predict pH on the basis of NP and MPA" (pg. 8). **It would be**

interesting to include phosphate results into the prediction model and no explanation is offered why these data where omitted.

In conclusion, the reviewed papers do not provide any evidence, which would suggest that the proposed use of the phosphate rock, together with the oxygen consuming bacterial growth in the root zone should not result in a successful reduction of acid generated.

4. COLUMN EXPERIMENT DETAILED DESCRIPTION

It is proposed to build a number of identical columns using the following materials:

- for cylinder body: Transparent extruded acrylic tubing, I.D. - 0.194 m, O.D. - 0.200 m, height - 0.560 m;
- for supporting plate: Clear acrylic sheet - thickness 0.01 m;
- for plate cylinder connection support circle: Clear acrylic sheet - thickness, 0.01m;
- for connections: Solvent cement UN 1133 3.2 and silicone;
- for tubing: Polyethylene tubing;
- for connection - Polypropylene connectors and dura clamp flow valves.

Two columns have already been built and are being tested for leaks and strength under the coal waste load.

4.1 PROPOSED CONFIGURATION OF TESTS

It is proposed to set up three configurations in the test columns . They are described below :

A) 0.15 m thick layer of code 30, coarse NPR and Long Harbour sand located at the bottom of a column (to assess changes in hydraulic conductivity) - three columns, Schematic 3;

B) 0.02 m thick layer of code 30, coarse NPR and Long Harbour sand located at he surface of the coal (to assess NPR-coal interactions) - three columns, Schematic 4;

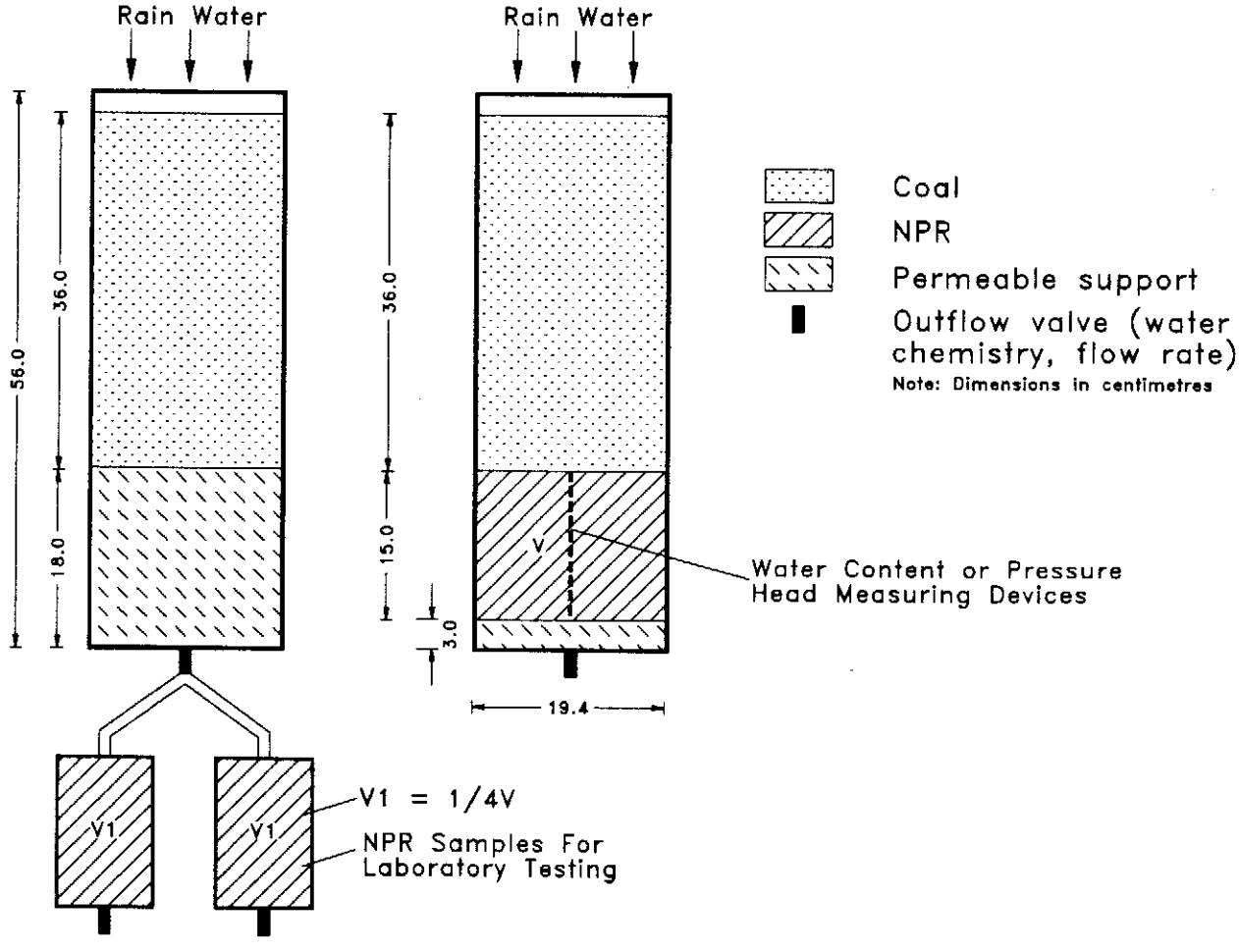
C) 0.02 m thick layer of code 30, coarse NPR and Long Harbour sand in the middle of the coal (to assess NPR-coal interactions) - three columns, Schematic 4.

Control columns (3) without NPR - each outflow will be used to water two undisturbed samples of NPR, Schematics 3 and 4.

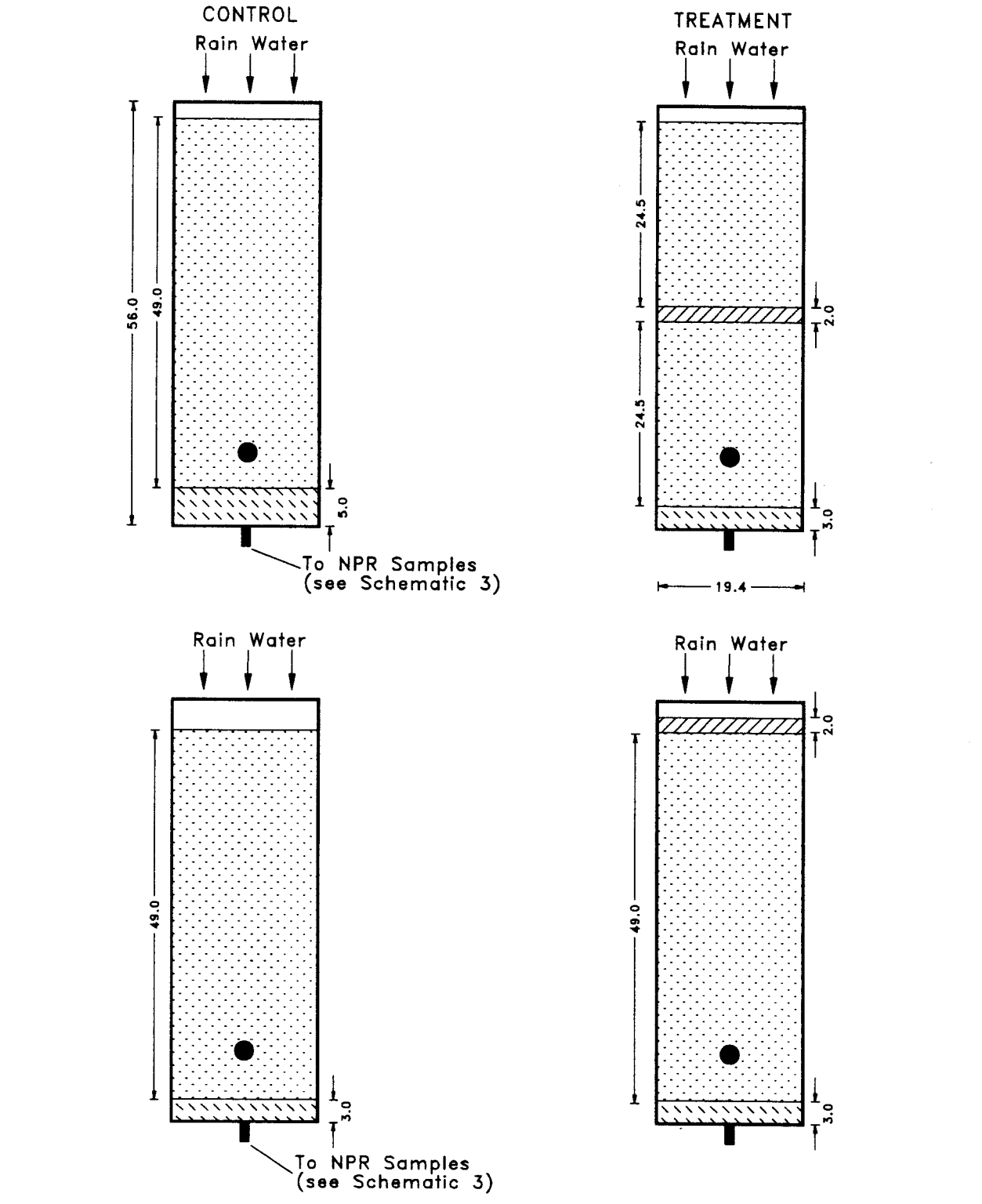
Total number of columns: 12

Volume of coal required: 12 x 15L = 180L

We require 10 (20 L) buckets with coal and 1 (20 L) bucket of Long Harbour sand. Since the experiment will have support a considerable weight, a frame was constructed to suspend the columns. This frame provides support which distributes the weight per square foot, so that it will not harm the Boojum laboratory. The steel frame and the distribution of the column weight have been approved by the building's structural engineer.



Schematic 3: Test configuration for hydrological properties.



Schematic 4: Test configuration for NPR - coal interaction.

4.2 PROPOSED OBSERVATIONS AND MEASUREMENTS

In this section the proposed the measurements and observations which need to be carried out are outlined. Range and number of proposed observations will be, in part, determined by the available budget in 1993. As became evident during the project that the experiment requires considerable resources. Funding for the oxigen measurements and Scanning election microscopic work was obtined from NRC National Research Council. In January the funds were apprved and some prelimnary results from one session at the SEM are reported.

4.2.1 Proposed measurements on the columns

The AMD generation process may be divided into three stages described as follows:

STAGE 1) water enters a coarse coal pile, percolates through; oxygen enters pile by diffusion, convection and dissolution in percolating water;

STAGE 2) Thiobacilli inhabiting sulphur source use water and oxygen for the sulphuric acid production;

STAGE 3) generated acid mixes with percolating water, and seeps out.

To assess effects of NPR on AMD it is proposed to measure and analyze:
for STAGE 1 and CONFIGURATION A:

- VOLUME of water percolating through the system.
  Location: outflow tubing.
  Possible equipment: to be determined.

- EVAPORATION (calculated in relation to environment temperature and humidity).

- CHANGES IN VERTICAL UNSATURATED HYDRAULIC CONDUCTIVITY of NPR layer in time as a result of biofouling and changes in chemistry (time domain reflectometry, thermocouples and tensiometers are considered for measuring water content or pressure head); unsaturated hydraulic conductivity will be calculated using computer code CRVFIT and tested in the lab using samples

from outflow of control columns and samples from treatment columns at the end of the experiment.

- NPR particle size distribution.
- NPR moisture content characteristics for fresh NPR and for material used during the experiment (NPR samples for laboratory testing, Schematics 3 and 4).

Columns will periodically receive the same amount of water.

For STAGE 2 AND 3 and CONFIGURATION A, B, and C, the following will be measured and analyzed.

- CHEMISTRY AND MICROBIOLOGY associated with AMD inside and on the surface of coal pieces.

Samples of coal and NPR will be analyzed using Scanning Electron Microscopy (SEM) and Electron Dispersive X-ray Analysis as described above.

For STAGE 1 and CONFIGURATION B and C, the following will be measured and analyzed:

- OXYGEN CONCENTRATION below NPR.

For STAGE 1, 2, 3 and CONFIGURATION A, B and C, the following will be measured and analyzed:

- TEMPERATURE inside the column.
- CHEMISTRY OF WATER percolating through the system.

Control columns will be observed in a similar fashion.

4.3 **INITIAL COLUMN DATA AND SCANNING ELECTRON MICORSCOPY**

Void ratio (control column): 30.27% which respresent likely loose mateial, ie. non compacted coal pile. It was expected that it will take some time until acid generation starts the control column was allowed to sit for some time before water was added. However 3.5L of rain water added on October 1, 1992 with a pH of 6.81, produced within one week (October 9th) an effluent with - pH 3.18. It was therefore concluded that the experiment can be started as soon as the coal arrives and further columns are constructed.

4.3.1. **Scanning electron microscopy studies**

The proposed inhibitory action of phosphate rock lays partly in the fact, that secondary mineral formation can inhibit the operations of heap leach piles. To have a comparison to the expected coatings which might be expected to from in the coarse waste rock pile, samples from Gibraltar mines have been obtained and are used as reference material fro the SEM studies of the pyrite surface.

Gibraltar Rock (background material) and coal form the control column were examined by scanning electron microscopy at McMaster University. Two sessions at the facily were made to test techniques for examination of rock surfaces in relation to morphology and chemical composition.

Surfaces of base metal waste rocks along with coal from the test column of the coarse waste rock were examined with the purpose of familiarization with surface morphology and for analysis (EDX) of surface materials to determine what if any secondary minerals are present and to relate the chemistry to surface morphology.

4.4 Methodology

Rock samples were chipped with a hammer. Pieces 1 to 4 cm in diameter were selected as these fit on stubs for SEM examination. Care was taken to minimise physical handling of the samples. The chips were handled with forceps. Immediately on sampling the chips were placed on sticky-tape within boxes to minimise physical disturbance and deposition of dust. Samples were collected while maintaining ambient temperature by chipping the rocks outside and placing the samples in a cooler kept at ambient temperature. This will be critical for future studies employing cryo SEM where preservation of biofilms is required. Removal of samples from ambient temperature and humidity may result in drying out of the rock surfaces and/or deposition of condensation water which will complicate interpretation of observations since water droplets are preserved in this SEM method.

The coal sample was removed from bewlow the surface layer of the laboratory test column which had received water two times, but no phopshate rock application.

Samples were mounted on stubs with a carbon-epoxy mixture (for effective electrical insulation) and coated with gold to a thickness of approximately 15 nm in a Polaron Cool sputter coater. Samples were examined in an ISI DS-130 scanning electron microscope. Samples were stored in a desiccator for future examination.

For analysis of surface materials, samples collected and mounted in the manner described above were coated with carbon in an Edwards evaporater carbon coater and subjected to EDX analysis with PGT System 4000 attached to the SEM. Image quality is much poorer with this set up but it enables electrons to reach the surface materials of the sample and cause emission of X-rays of wavelengths characteristic of the element. The X-ray spectra were collected and analyzed to determine the composition of original rock materials and secondary surface minerals. Direct quantification of elements or minerals is not possible except on

perfectly flat samples because corrections for absorption require accurate determinations of X-ray path lengths (Blake, 1990). Fe:S ratios were used to determine whether iron sulphides are pyrite or other compounds (Fe_2S, FeS) which are undoubtedly secondary minerals. The ratio of the major peaks for what was clearly a pyrite crystal (C14) was <0.5 and in the study of Welton, ranged from 0.3 to 0.7. Deviations from this ratio indicate that other iron and/or sulphur compounds are present.

Gibraltar rock: The Gibraltar rock material is believed to have secondary mineral coatings which have inhibited Cu oxidation in a leach heap. Gibraltar rock (Plate 1) exhibits a very open or porous structure. Flaky material is believed to be aluminum silicates (suggested by subsequent EDX studies). A variety of surface materials (e.g. the hypha-like bodies in Plate 1) are believed to be secondary minerals.

Examples of EDX spectra for Gibraltar rock are shown in Figures 1 and 2. The data for all spectra are summarised in Table 1. The EDX data (Table 1) indicate an abundance of Al, Fe, S and Si at most points examined. An example is shown in Figure 1. This is indicative of SiO_2, aluminum silicates and ferrous sulphides. The very high Fe:S ratio for GIBH indicates that ferric hydroxides predominate in this sample. This is undoubtedly a secondary mineral. The Fe:S ratios of GIBB, GIBD and GIBF (Figure 1) are 1.2, 1.3 and 1.0 respectively. Although the peak ratio cannot be directly equated to the molar ratio, they do give a clear indication of for example how reduced iron sulphides are and whether they are pyrite or FeS. Pyrite gives an Fe:S peak ratio of approximately 0.5. Ratios of 1 and above suggest that FeS may be present, undoubtedly another secondary mineral. The association of Na and K with Fe and S at these points suggests that jarosite ($AFe_3(SO_4)_2.(OH)_6$ where A may be Na^+, K^+ or NH_4^+), a secondary mineral, is present. Phosphate was present at five of the thirteen locations examined and may be a constituent of another secondary mineral. The only cations always associated with P are Al and Fe. Either or both of these could form insoluble phosphates.

Coal and coal precipitates: Samples of precipitates from laboratory columns of coal with were examined by SEM with EDX. These precipitates exhibiting a range of colours provide an opportunity to link physical appearance (colour) to chemistry (EDX spectra). Examples of spectra are shown in Figures 3 and 4. An orange precipitate (COALA) contains a large percentage of sulphur but also Al and Mg suggesting the presence of $MgSO_4$ and Al. The grey-green precipitate also contained much sulphur but also Fe, K and Mg. The high percentage of S in both precipitates indicates that elemental sulphur is present.

Summary SEM studies: The two SEM sessions achieved the primary goal of testing methodology for examination of rock surface morphology and through EDX analysis to characterise primary and secondary minerals. Much experience was gained both in handling the sophisticated equipment and in interpreting images and data produced. Materials from Gibraltar rock and coal samples were examined but were sufficient to demonstrate that the McMaster facility can be used to examine rock surfaces. Secondary minerals were observed. In particular, the presence of P on Gibraltar rock bodes well for the development of phosphate-based, oxidation-inhibiting layers on waste-rock surfaces.

Plate 1: Scanning electron micrograph of Gibraltar rock.

Sample	Scan	Description	Magn.	Element									Fe:S
				Al	Ca	Fe	K	Mg	Na	P	S	Si	
Gibraltar Rock	GIBA	Exposed surface	105	*		**	*	*		*	**	*	0.7
	GIBB	"	105	**		*	*		*		*	**	1.2
	GIBC	"	209	*		**				*	**	*	0.72
	GIBD	"	209	**	*	**	*	*		*	**	**	1.3
	GIBE	"	158	**	*	*				*	**	*	0.57
	GIBF	"	315	**	*	**	*		*	*	**	**	1
	GIBH	"	38			**					*		9.6
	GIBI	"	76	**		**					**	*	0.61
	GIBJ	"	76									**	
	GIBK	"	76	**								**	
	GIBL	"	76	*	*	*	*				*	**	0.25
	GIBM	"	76	**			*		*			**	
	GIBN	"	76	*	*	*					*	**	0.1
Pert pile coal	COALA	Orange precipitate	38	*				*			**	*	0
	COALB	Grey-green precipitate	38			*		*	*		**		0.1
	COALC	Grey-green precipitate	38			*		*	*		**		0.03
	COALD	Non-oxidised coal	504	*	*	*	*				*	**	0.27
	COALE	Non-oxidised coal-crystal	92	*	*	*					**	*	0.15
	COALF	Non-oxidised coal-next to D	92	*	*	*					**	*	0.16

** major peak

* minor peak

Table 1: Elemental composition of EDX scans

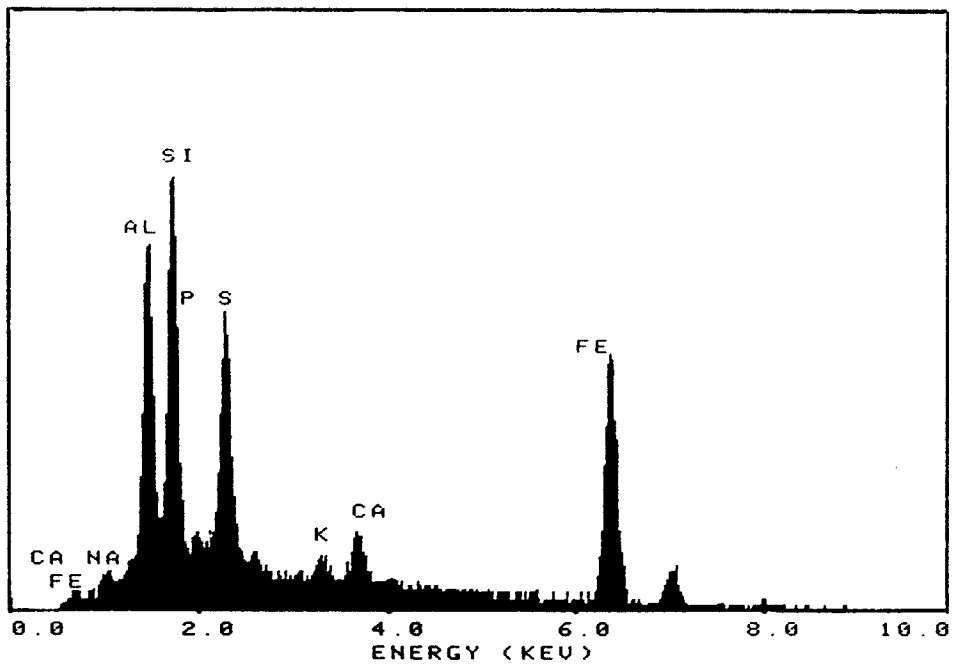


Figure 1: Gibraltar rock - EDX scan.

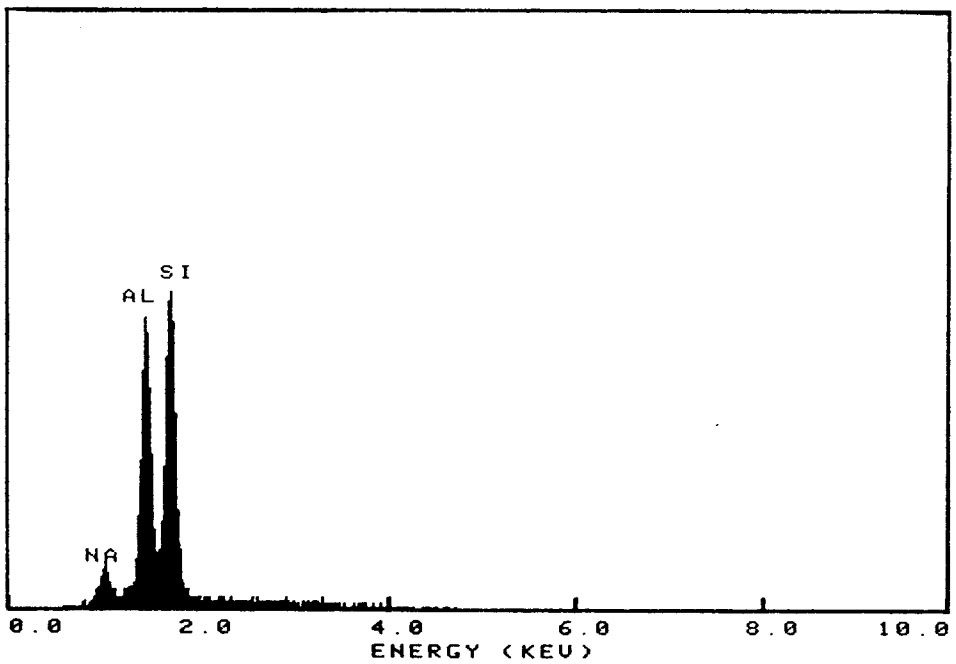


Figure 2: Gibraltar rock - EDX scan.

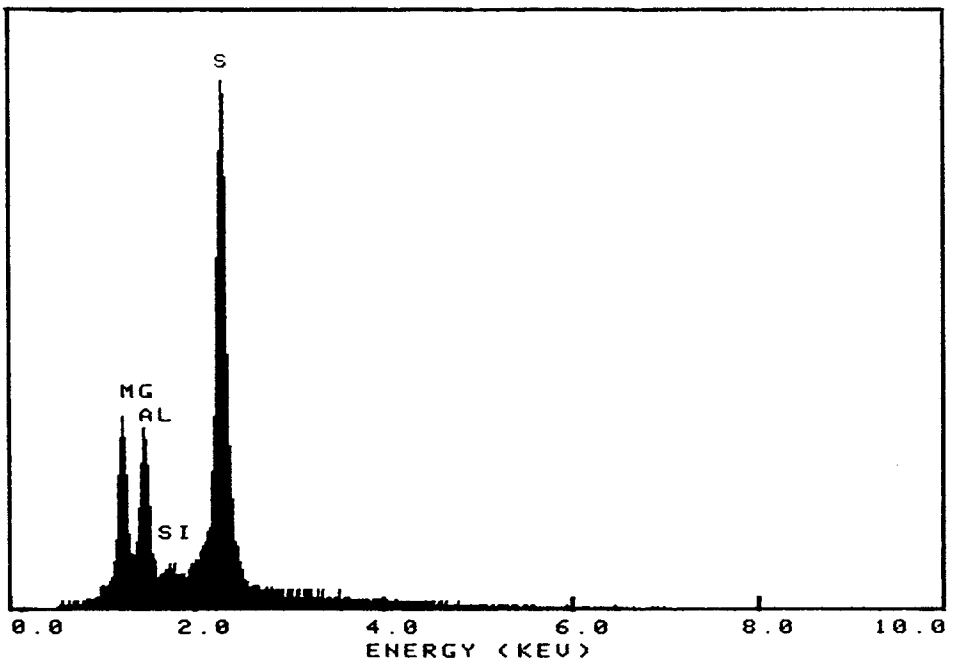


Figure 3: PERD pile coal, orange precipitate - EDX scan.

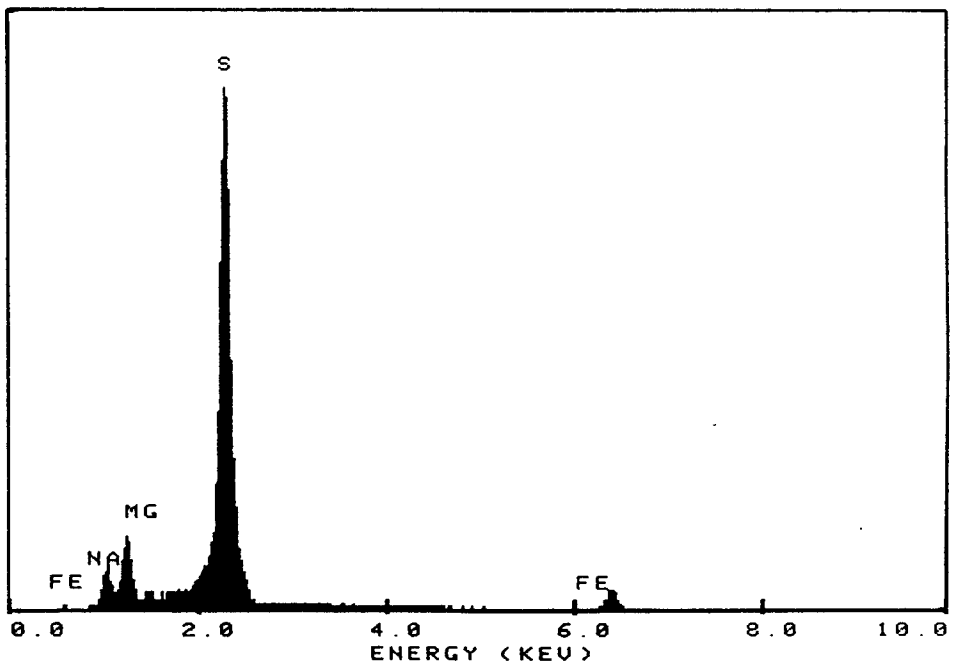


Figure 4: PERD pile coal, grey-green precipitate - EDX scan.

5. CONCLUSION AND RECOMMENDATIONS

From the review of the litterature and the prelimniary work carried out on the SEM facility with the funds from the National Research Council suggest,that NPR might indeed provide the inhibitory action on acid generation in coal piles. It is recommended that the column experiment be implemented.

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VJPP Coal Waste-Phosphate Rock Laboratory Column Experiment

Progress Report

January 1994

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VJPP Coal Waste-Phosphate Rock Laboratory Column Experiment

OBJECTIVE

To determine, under laboratory conditions, the effect of phosphate rock and its mode of application on the inhibition of oxidation of coal waste from the Victoria Junction Coal Processing Plant PERD pile No.5.

1.0 INTRODUCTION

Phosphate rock has been successfully tested in the laboratory with other mine tailing materials to reduce the production of acid mine drainage (AMD).

The phosphate rock has been shown to inhibit acid generation and neutralise the acid produced by,

a) the formation of a pan of precipitates which inhibits passage of air,

b) coating surfaces of pyrite-rich materials to physically and chemically inhibit reactions, and

c) the calcite and other minerals contained in the rock that will neutralize acid present in the effluent.

Long Harbour Sand (LHS), a high grade phosphate rock, formerly used by Electric Reduction as its feed to an elemental phosphorus production plant, is a local source of limited tonnage. It has been added to one of the PERD coal piles at the Victoria Junction Coal Processing Plant. The material was applied to PERD pile #5 as a layer with an average thickness of 10 cm, with this being topped with more waste coal.

It is anticipated that a pan will form within or just below the phosphate rock material when the phosphate comes in contact with AMD. The column experiment will establish

whether such a pan forms under laboratory conditions, and will examine the effect of the phosphate material on both the chemistry of the drainage effluent leaving the column and on the surface morphology and chemistry of the coal waste where oxidation and AMD generation normally occur.

The column experiment will also compare the effects of a discrete phosphate rock layer with that of a surface mixture of coal waste and phosphate rock. This could provide increased contact between the phosphate rock and coal waste which may assist in formation of a pan and the inhibition of oxidation.

Additional Columns were also set up with another grade of phosphate rock, Texasgulf's natural phosphate rock (NPR). This is a much coarser material than the Long Harbour Sand and may react differently in the presence of coal waste. This material is being tested as the long-term availability of Long Harbour Sand is uncertain.
The chemical grade and screen analysis of these two materials is reported in the appendix.

2.0 THE DESIGN

The two types of phosphate rock (NPR and LHS) were tested in duplicate, in two configurations for the addition of the phosphate to the waste coal, as shown in Schematic 1, with two Control columns (zero phosphate). The 10 column treatments, are summarised in Table 1.

The two configurations are,
a) a 5 cm layer of phosphate buried under 15 cm of coal, similar to the PERD pile set up, and

b) a 15 cm surface mixed layer comprising a 2:1 ratio (v:v) of coal to phosphate rock. This mixture will provide more contact between the coal and phosphate rock, which may form precipitates locally where acid is generated. This configuration could readily be implemented in the field with conventional tilling equipment.

Underlying the phosphate rock or coal/phosphate rock mix is a 27-32 cm layer of coal. Below the coal waste, there is a layer of polystyrene chips with a void space of 840 mL.

The column overflow is set just below the polystyrene-water interface.

3.0 THE MEASUREMENTS

Distilled water was added to the columns, once a week for six weeks, then every two weeks, at a rate equivalent to the rainfall measured at Sydney Airport, the nearest meteorological station to the Victoria Junction Coal Processing Plant. The ten year average of precipitation was found to be 1480 mm of rain, which was calculated as 840 mL/column/week for the 19.5 cm diameter columns.

Samples for chemical analysis were collected and measurements made as soon as possible, generally within 3 hours. Effluent from the column will displace standing water at the base of the column. The effluent sample was refrigerated prior to analysis.

Acidity titrations were carried out using a Metrohm Titrino autotitrator with NaOH as the titrant. This will give a measure of total acidity released from the column and also the general chemical composition of that acidity (from the shape of the curve). Acidity is determined as the mg/L equivalent of calcium carbonate required to raise the pH to 8.3.

In addition to acidity, measurements have been made of the pH, the redox potential

(Eh) which reports the level of oxidation or reduction of the solution and electrical conductivity reports the quantity of dissolved salts present. The weekly results will effect curves for Figures 1 to 13.

4.0 RESULTS

4.1 CONTROL COLUMNS

Oxidation was first detected by the appearance of orange precipitates on coal surfaces of the control columns (Columns 9 and 10), after 8 days. Acidity was present in the first effluent samples at 7 days from the set-up.

At 21 days, an increase in acidity, conductivity and Eh and a decrease in pH indicated an increase in oxidation. Thereafter, there was a dramatic decline in pH (Figure 1), a rapid rise in acidity (Figure 2) a steady rise in conductivity (Figure 3). Eh was initially about +300 mV and rose with the acidity generation to a steady value of about +750 mV (Figure 4).

The increase in acidity and decline in pH was accompanied by the appearance of an orange, ferric hydroxide precipitate in the effluent. In fact, a faint orange tinge was evident before increase in acidity and decreases in pH were evident indicating that oxidation was locally occurring.

From 28 days, the effluent became clear and orange brown. Below pH 3, precipitation of ferric hydroxide ceases. The colour became more intense with time, acidity and concentration of the dissolved ferric iron increased.

By 35 days, acidity of effluent samples had risen to over 700 $mg.L^{-1}$ equiv $CaCO_3$ (Figure 2). The shape of the titration curves at this time (Figure 6) confirms that much

of the acidity is attributable to ferric iron, the hydrolysis of which is responsible the flat portion of the curves at pH 2.9-3.6.

By 120 days, acidity had risen to around 25000 $mg.L^{-1}$ equiv. of $CaCO_3$ (Figure 2). Total acidity generated at this time is equivalent to 3-4 g/column/day.

4.2 LONG HARBOUR SAND

4.2.1 LHS LAYER

In Columns 1 & 2 with a 5 cm layer of Long Harbour Sand, the pH of effluent was initially higher than in the Control (Figure 1). However, conductivity was higher (Figure 3) and both acidity (Figure 2) and alkalinity (data not shown) were higher than in the control. This was attributed to dissolution and washing out of salts from the LHS.

There was no increase in acidity or decline in pH of the effluent until Day 52 Column 1 or Day 77 Column 2 (Figure 2). Clearly, in this configuration, the Long Harbour Sand was inhibiting oxidation and acid generation by the column. Oxidation was certainly occurring in places since orange patches (ferric hydroxide precipitates) were visible on the coal surfaces at 8 days, as in the other columns.

After 52 days for Column 2 and 77 days for Column 1, there was an increase in acidity (Figure 2), conductivity (Figure 3) and Eh (Figure 4) and a decline in pH (Figure 1). However, the rates of change were much slower than in the Controls.

From 91 days, the pH was fairly steady at around 2.7-2.9 near the critical pH required for precipitation of $Fe(OH)_3$.

After 120 days, acidity of the effluent (3023 mg/L, mean of 2 columns) was only about

12% of that of the Control (mean of 25520 mg/L).

It was observed that even at 120 days, the first 200-300 mL of effluent leaving Column 1 was clear and without the orange colour. This fraction was also accompanied by an H_2S smell, indicative of sulphate reduction which only occurs in the absence of oxygen and in the absence of bacterially reducible ferric hydroxide. This was not observed in other columns and indicated that the Sand band was a barrier to air transport.

This was also indicated by the slow percolation rate (Figure 7). At this time, it took more than 11 minutes for the first 300 mL of added water to pass through the Columns compared to a mean of 2.8 minutes for the other columns.

4.2.2 LHS MIXTURE

The mixing of the Long Harbour Sand with the coal (Columns 7 and 8) resulted in very different effluent quality from the layer treatment. There was a slight delay in increase in decline in effluent pH (Figure 1) and increase in effluent Eh (Figure 2). From Day 35, the readings of pH (Figure 1) and Eh (Figure 4) were similar to those of the controls.

By 120 days, acidity was greater in Column 6 than in the controls (Figures 2 and 6); conductivity was also greater. The main difference in the titration curves are a greater flat section at pH < 3 which corresponds to the hydrolysis of ferric iron and to a lesser extent, a flattening at pH > 7.5, attributable to precipitation of calcium and magnesium. At this time, daily acidity production was similar to that at 104 days indicating that rates have reached a maximum. It is not known whether the Control will achieve the same rate.

4.3 TEXASGULF NATURAL PHOSPHATE ROCK

4.3.1 NPR LAYER

In the effluent of columns with a 5 cm layer of NPR (Columns 3 & 4), the patterns of changes in acidity (Figures 8 and 9), pH (Figure 10), conductivity (Figure 11) and Eh (Figure 12) were very similar to those of the control columns (Columns 9 and 10). However, 120 days after set-up, acidity was greater than in the controls (Figures 8 and 9). The titiration curves indicate a longer flat section than the controls at pH 2.9 - 3.5 which indicates a greater concentration of dissolved ferric iron.

From day 63, pH was steady at 2.1 - 2.3, Eh around +650-700 mV and conductivity 7-10,000 umhos/cm.

From day 104 the conductivity was higher than that of the Control. This was associated with the greater acidity and therefore Fe and SO_4^{2-} in solution.
The percolation time taken for 300 mL of effluent to leave the column after water addition was similar to that of the Control (Figure 13).

4.3.2 NPR MIXTURE

In Columns 7 & 8, the NPR was mixed with coal as a 15 cm layer above the waste coal. The chemistry changes were similar in time and quantitatively to those of the NPR layer columns (Figures 8-13).

5.0 OVERALL DISCUSSION

Initiation of oxidation of pyrite in coal and the generation of acid mine drainage AMD from the experimental columns was rapid (22 days in the control columns). The acidity of the AMD increased to a fairly constant rate at 120 days.

In the layer configuration, Long Harbour Sand was effective in inhibition of AMD generation from the columns both in terms of a delay in the initiation of acid generation and a decrease in the rate of acid generation in comparison to the Control system values and the three other phosphate rock treatments (80-90 % inhibition).

The configuration was not totally effective and continued observations will determine whether the inhibition increases or diminishes with time.

Observations of the column showed a pronounced band of iron phosphate (grey) and ferric hydroxides (orange) at the upper and lower boundaries of the layer. Some precipitates were also evident within the layer indicating that precipitates are rapidly formed on contact between AMD and the Long Harbour Sand. These precipitates undoubtedly contributed to the decreased permeability of the columns (Figure 6).

At Day 120, there was very little orange ferric hydroxide precipitate in the lower part of Column 1 and much less in Column 2 than in the Control. This was a reflection of the inhibition of oxygen transport by the LHS layer. Decreasing the oxygen supply to the coal inhibits oxidation and result in a decrease in the overall acidity in the column effluent.

The other phosphate rock treatments delayed the onset of AMD generation a little. The initial delay may be due to wash-out of neutralising agents in the phosphate rock (as indicated by higher conductivity, Figures 3 and 11). However, by 104 days rates of acidity generation were greater for 5 of the 6 columns than the controls. A possible explanation was that the phosphate rock was supplying the oxidizing bacteria with phosphates and other nutrients which may otherwise be limiting. A detailed analysis of the effluent chemistry and also examination of the coal surfaces when the columns are dismantled may provide an explanation.

6.0 THE FIELD TEST

The field PERD pile was set up by Nolan-Davis at the Victoria Junction Coal Processing Plant in the late fall of 1992.

Chemistry data on effluent samples for June 11, June 29 and August 6, 1993 are summarised in Table 2, the complete data is shown in the Appendix.

The first sample was collected soon after the spring thaw. The water chemistry indicates that AMD generation had not commenced as the conditions in the pile were unfavourable for pyrite oxidation. The temperature of the pile at this time was too low for much biological activity.

By June 29, the situation had changed dramatically. The pH of the water had dropped to 2.3, the iron risen to 1360 mg/L and substantial content of other heavy metals (manganese, copper and zinc) as well as aluminum (246 mg/L).

The third sample was collected in high summer when temperatures within the pile were high and therefore favourable for biological oxidation. However, the water quality had substantially improved since the late-June sampling. The pH had only risen to 3.4. The iron content of the effluent had dropped to 6.72 mg/L and concentrations of aluminum, manganese, copper and zinc and sulphate had substantially declined. This together with the appearance of low levels of phosphate indicate that the Long Harbour Sand had started to act.

The pH of the effluent was sufficiently high for precipitation of ferric hydroxides with plus ferric phosphate at the LHS layer accounted for the dramatic decline in iron concentration.

The field configuration of coal and LHS is comparable to that in columns 1 and 2 in the

laboratory experiment. In both cases, the LHS is clearly having considerable effects on the overall generation of AMD from the coal. Whether the observed effects are directly due to phosphate chemistry or indirectly to the generation of a permeability barrier has not been shown in the field. However the reduced flow rates and reducing conditions observed in Column 1 of the laboratory experiment indicate that the LHS can form a barrier to both water and air penetration.

7.0 FUTURE STUDIES

Monitoring of the columns will continue. and additional information on the chemistry of effluent will be collected.

It is important to note that at the end of the 120 day period, the rates of increase in acid generation had slowed down in all of the columns. A steady rate of acid generation was being achieved and from the acid generating potential of the coal, the time required to complete acid generation will be estimated. The acidity generating potential of the coal in all the columns should be the same. The long term results of the test columns will determine whether and how long the phosphate rock materials can delay or prevent AMD generation.

At the end of the study, the columns will be dismantled and samples from different locations taken for determination of the presence, quantity and nature of precipitates. This will involve light and electron microscopy studies coupled to EDX analysis to determine composition of surface materials. Chemical removal of precipitates will also be carried for quantification of precipitates. In all of these studies control samples maintained under nitrogen (to prevent oxidation) will be studied for comparison.

More chemistry data and samples will be collected from the field experiment to determine that the same processes are occurring in the piles as in the columns. These comparisons will help fine-tune the design of future treatment piles.

Fig 1: Long Harbour Sand pH

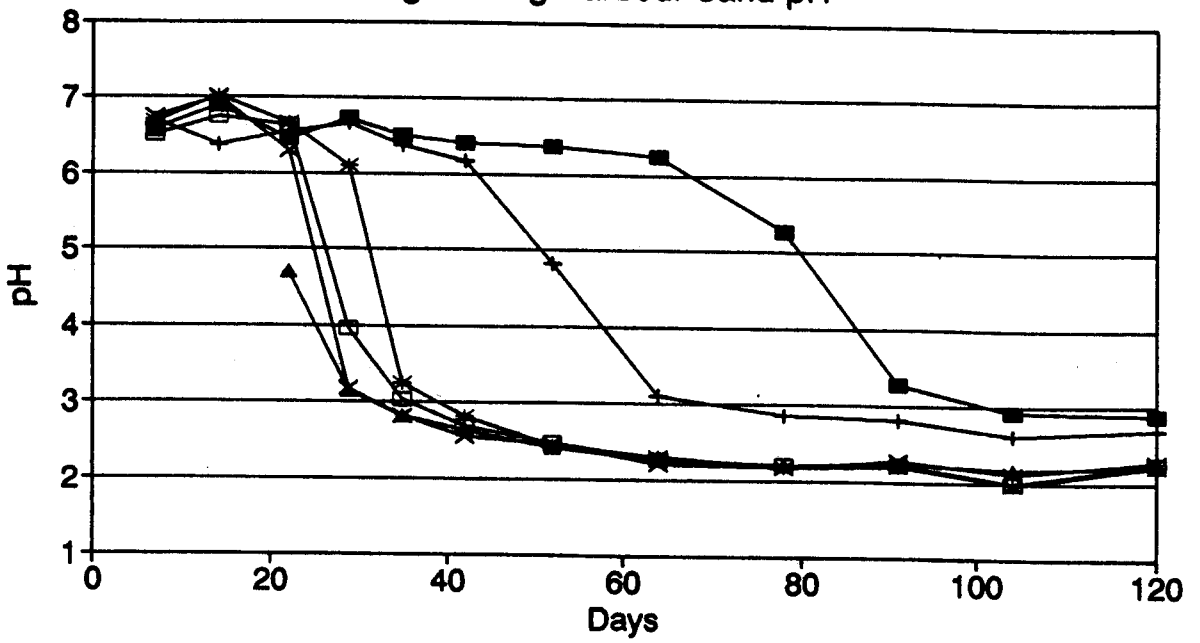


Fig 2: Long Harbour Sand Acidity

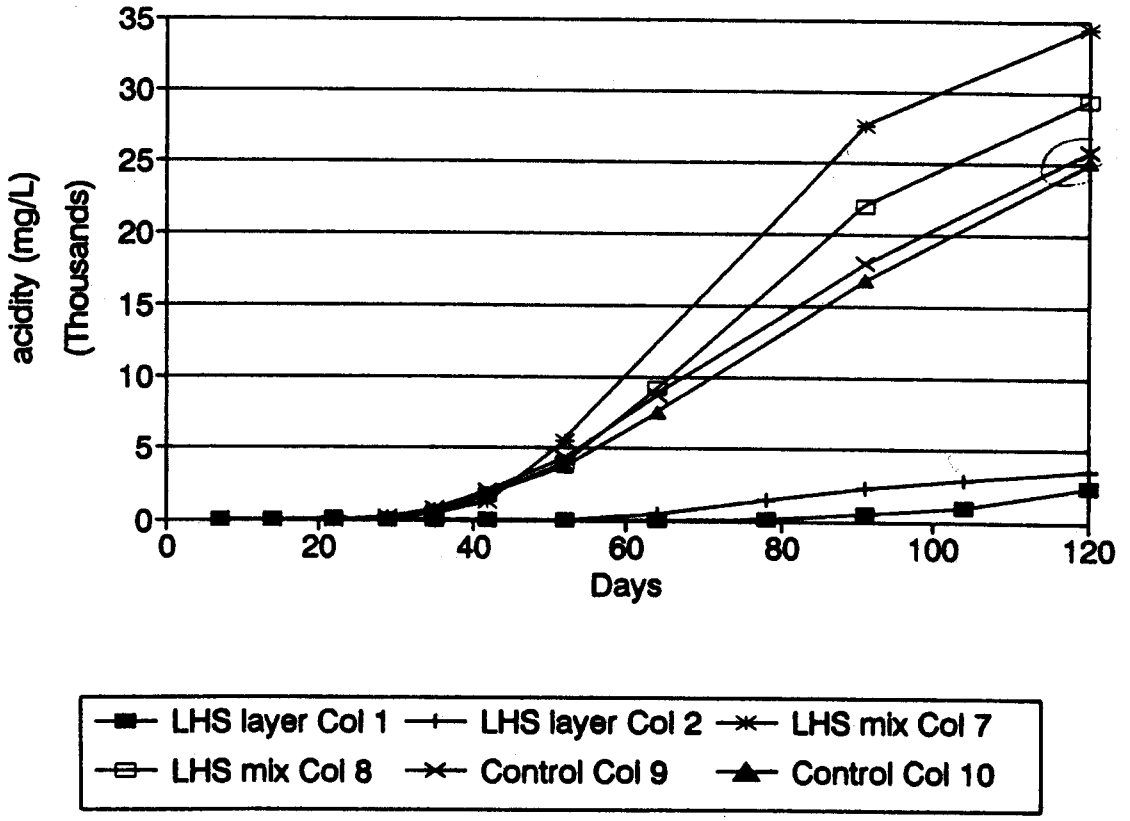


Fig 3: Long Harbour Sand Conductivity

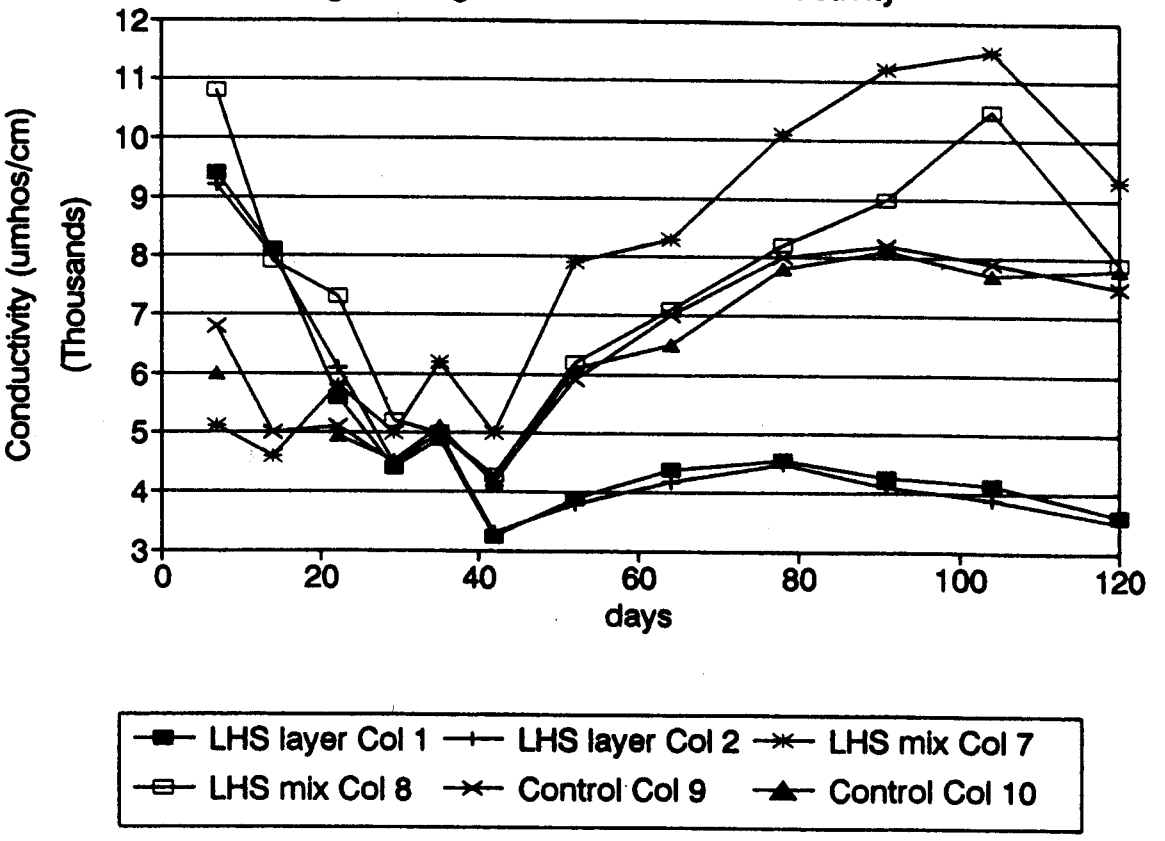


Fig 4: Long Harbour Sand Eh

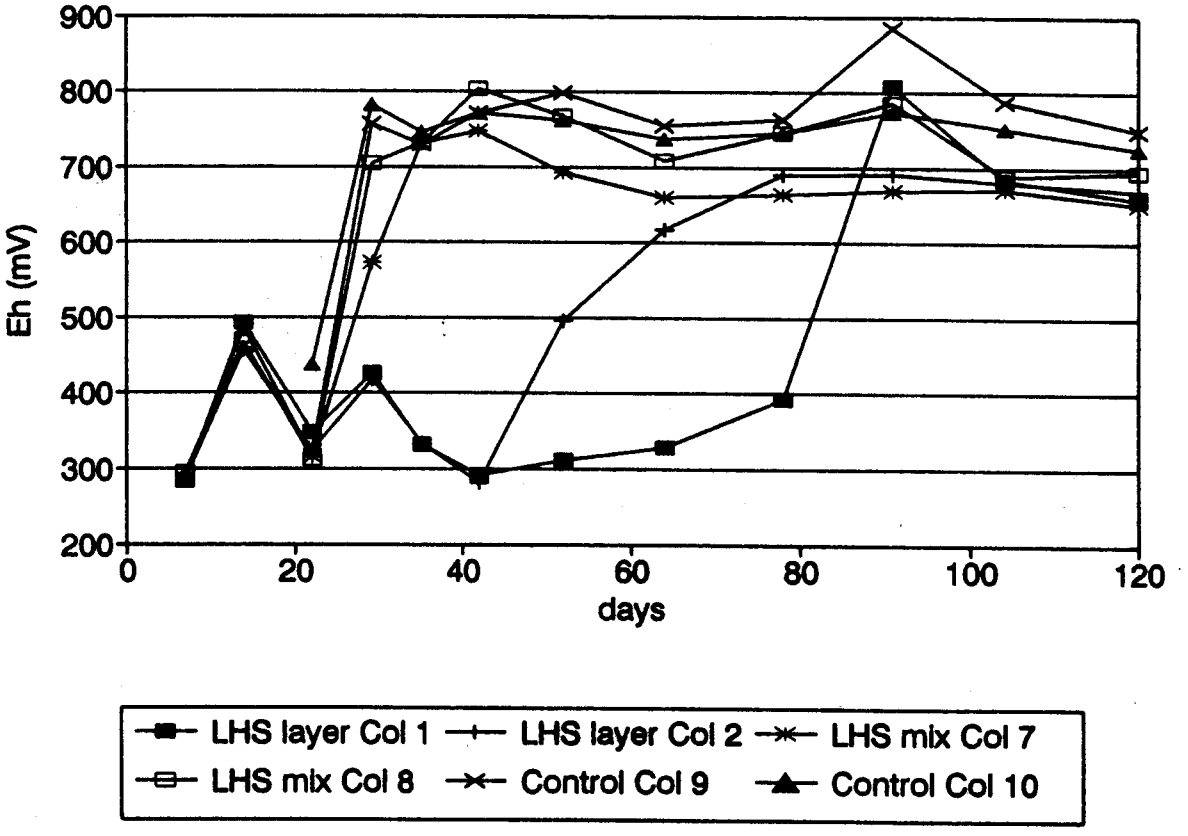


Fig 5: Long Harbour Sand Mix
Titration Curves - 120 days.

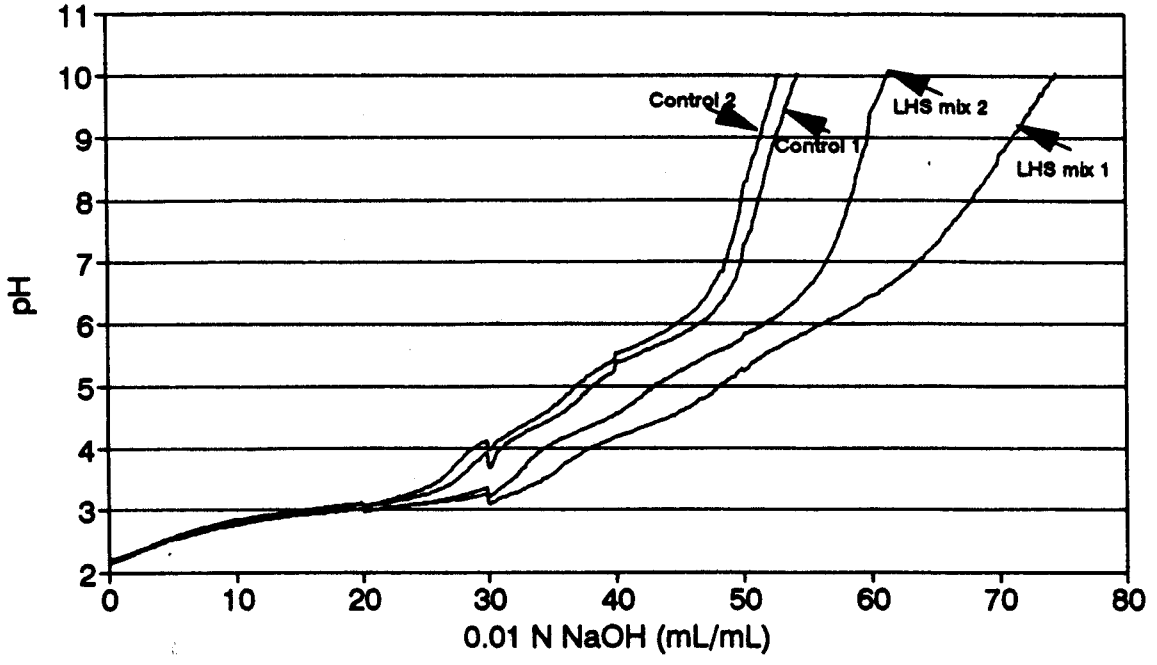


Fig 6: Long Harbour Sand Layer
Titration Curves - Column 1

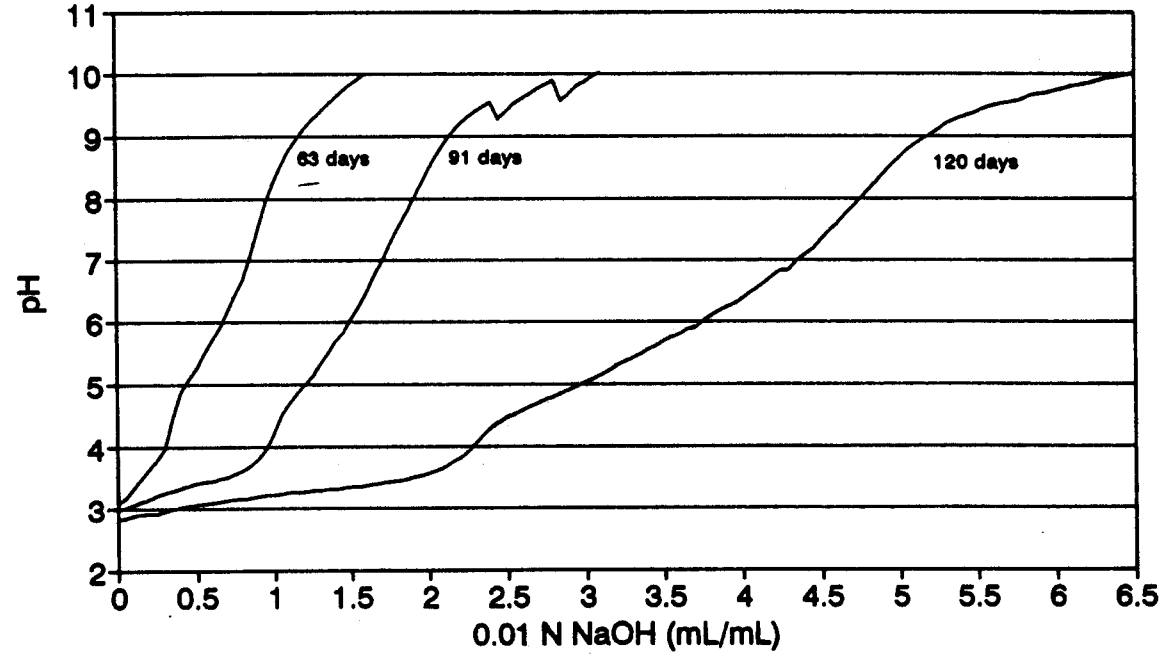
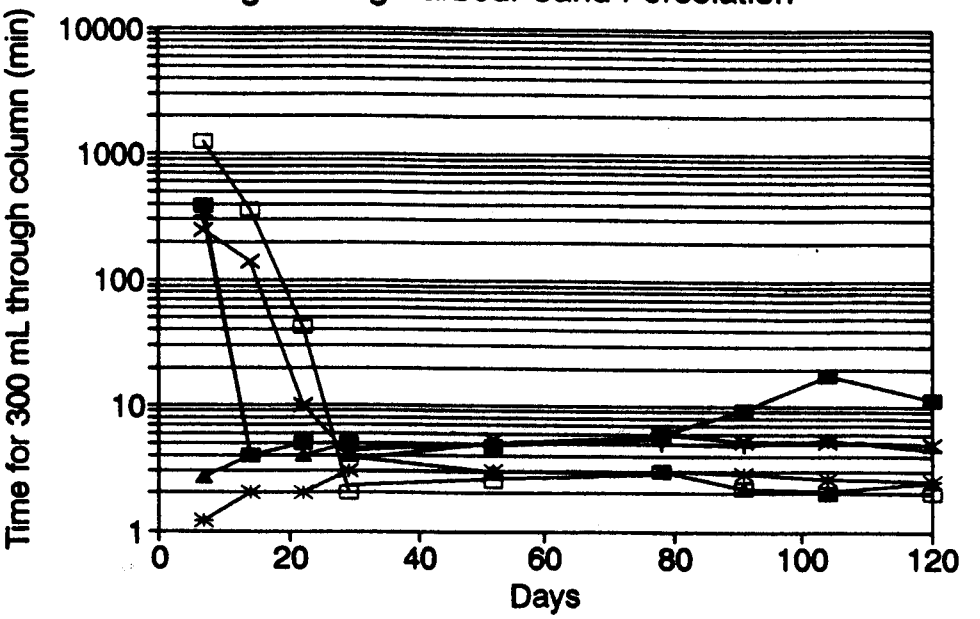


Fig 7: Long Harbour Sand Percolation



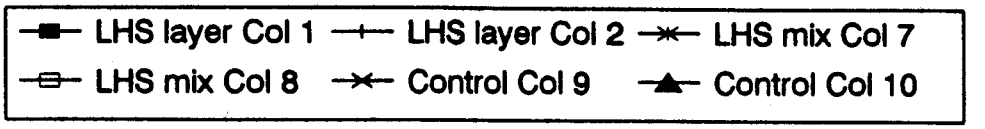
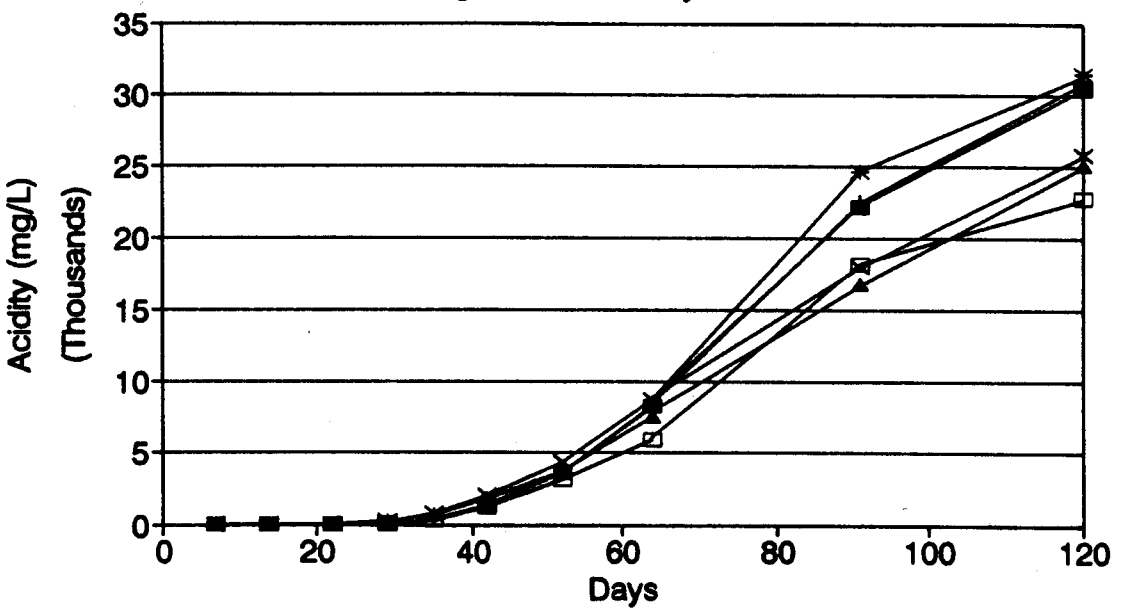


Fig 8: NPR Acidity



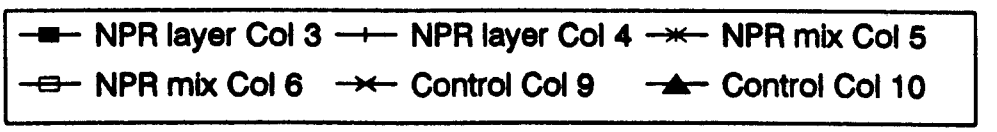


Fig 9: NPR Layer
Titration Curves - 120 days

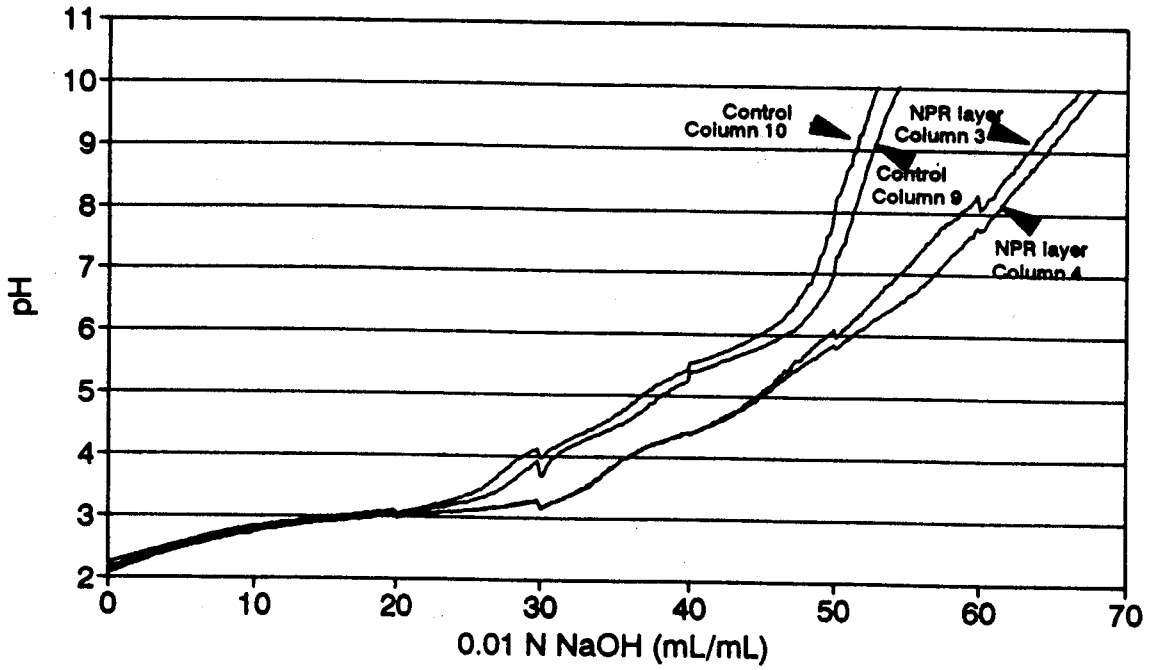


Fig 10: NPR pH

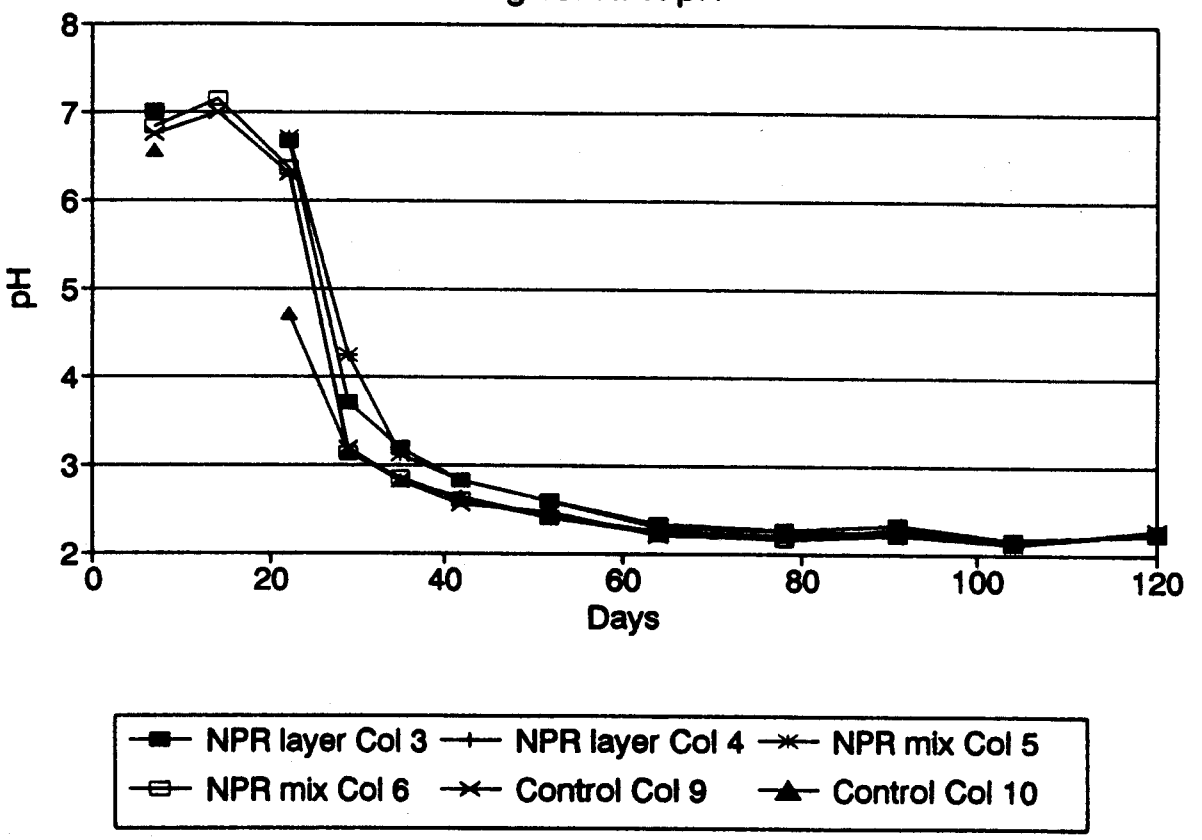


Fig 11: NPR Conductivity

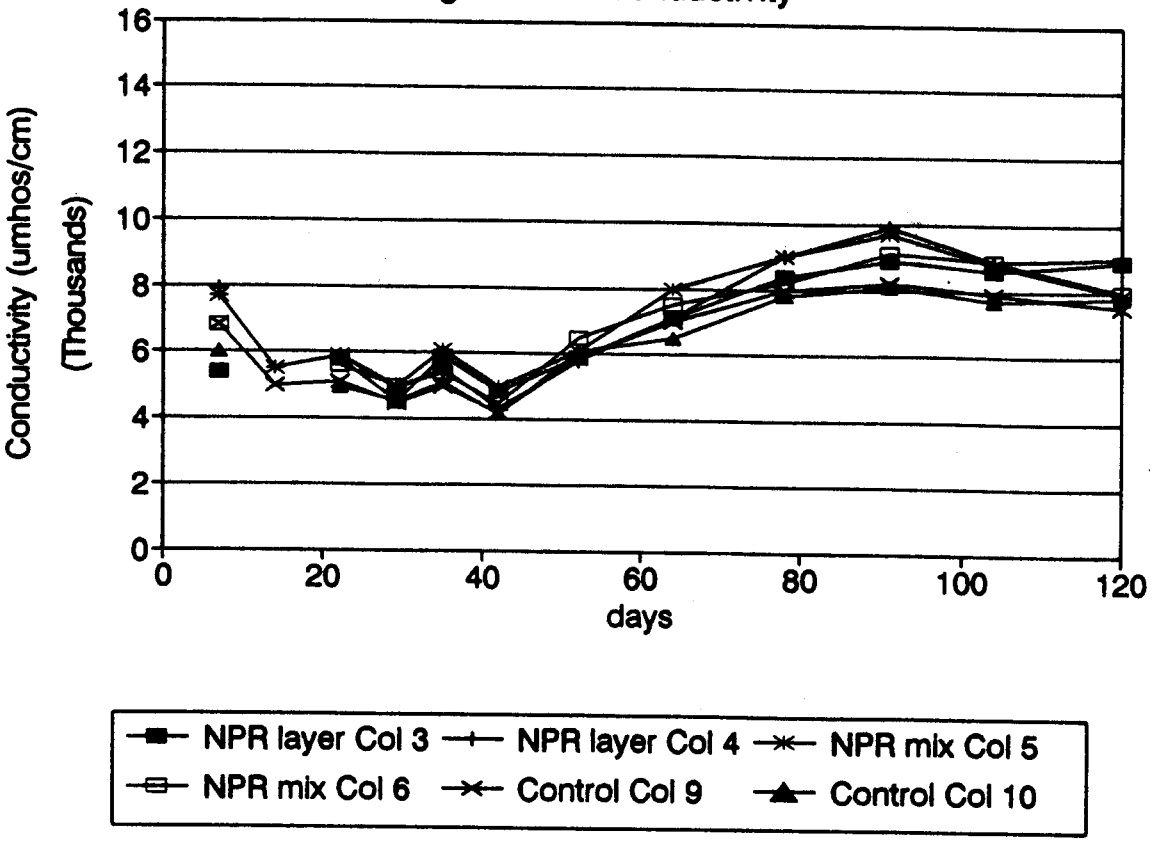


Fig 12: NPR Eh

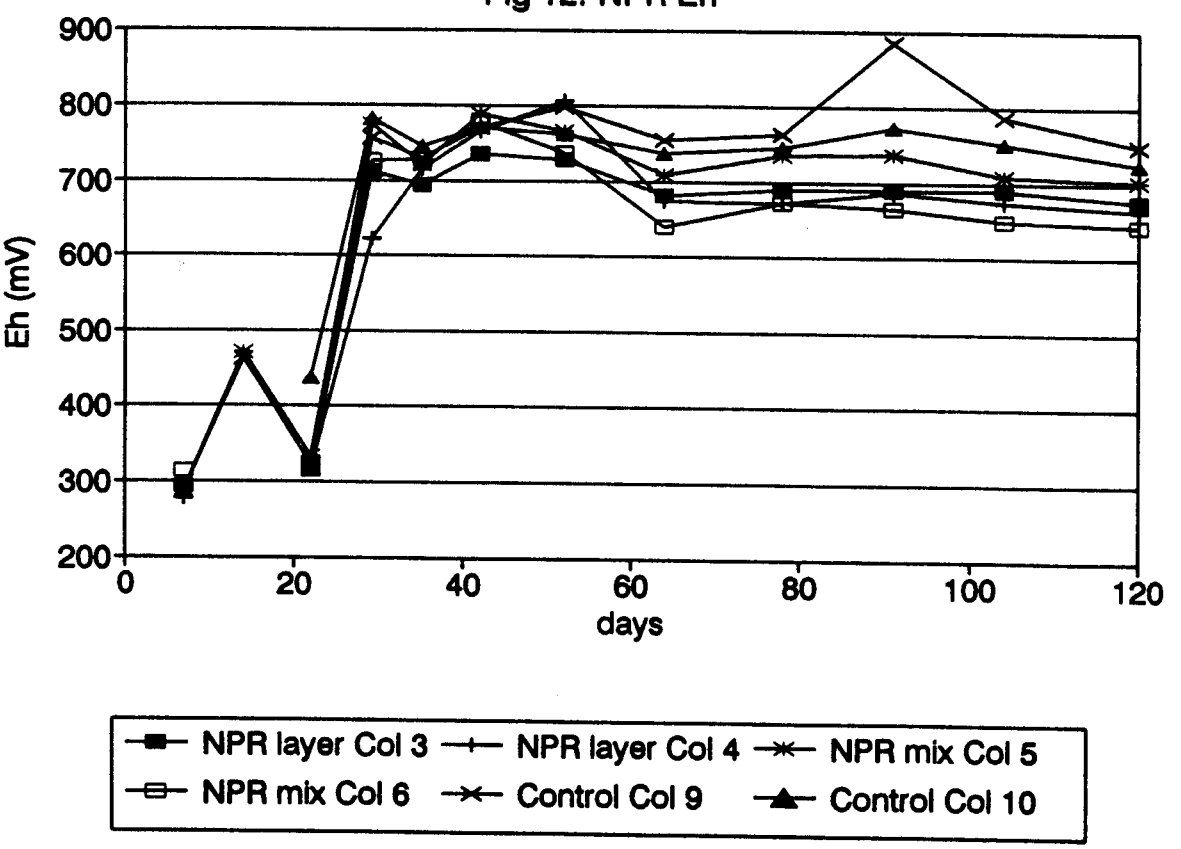


Fig 13: NPR Percolation

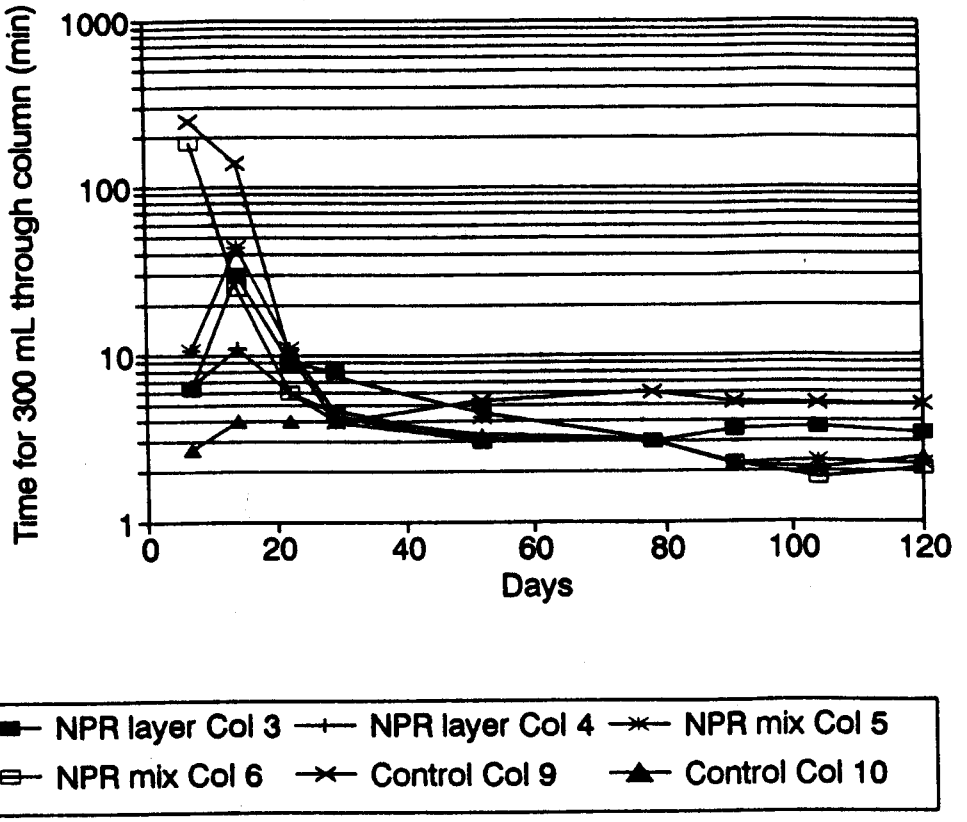


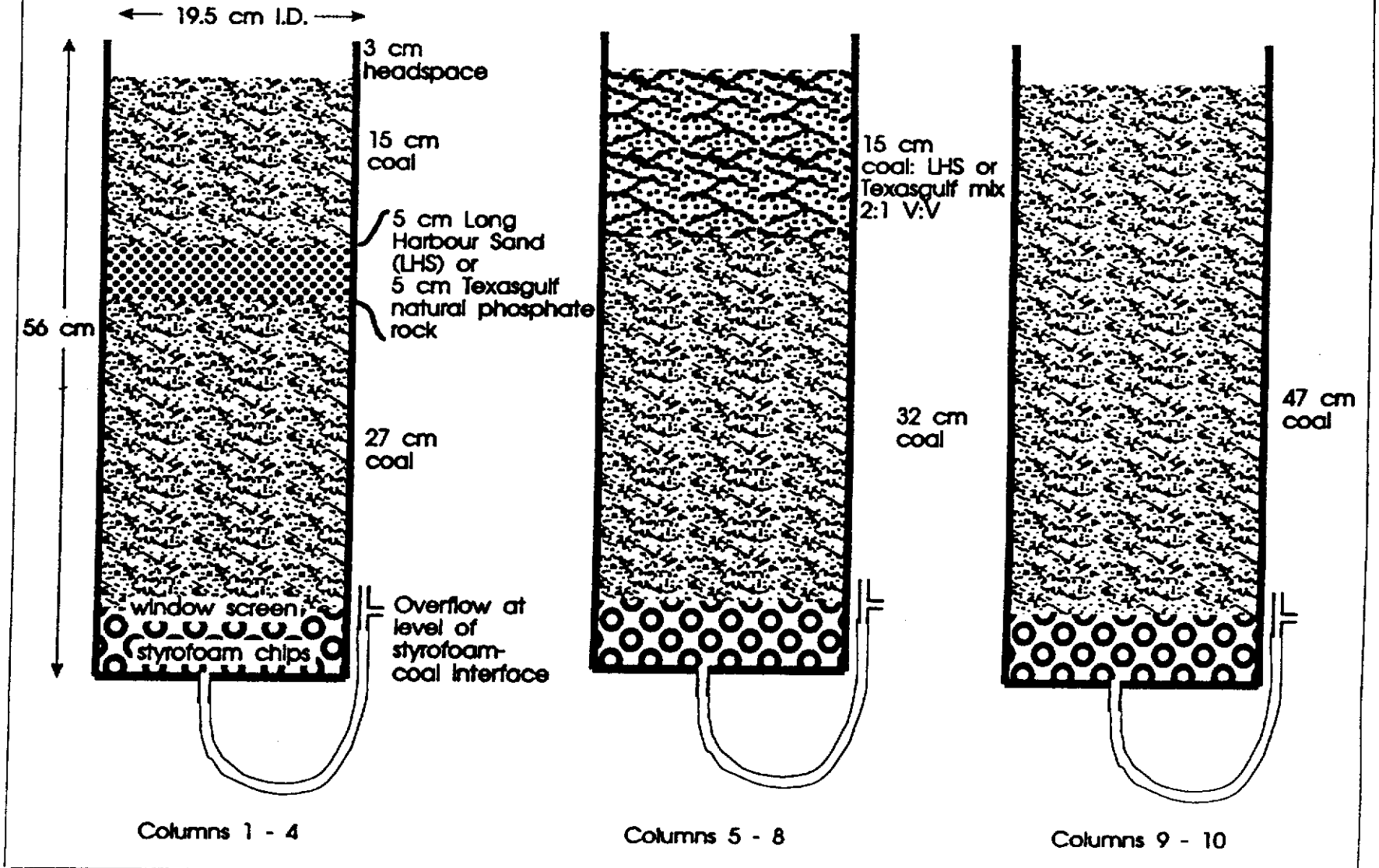
Table 1: Perd Pile Coal/Phosphate Rock Column Experiment-Experimental Design

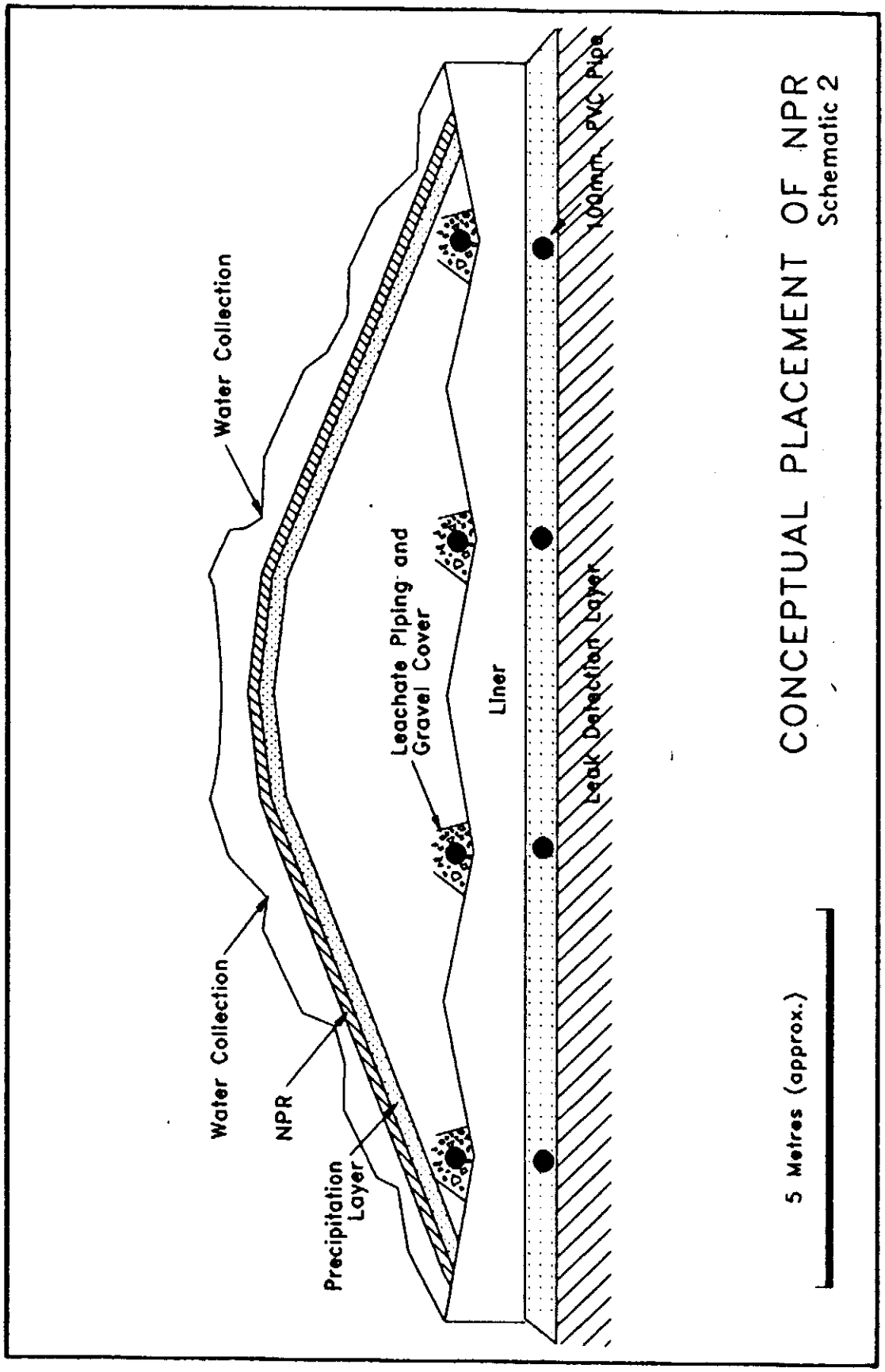
Column	Polysturene chips cm	Bottom Coal Layer cm	Phosphate Rock Type	Phosphate Rock Layer cm	Top Layer	Top Layer Depth cm	Top Space cm
1	8	27	Long Harbour	5	coal	15	1
2	8	27	Long Harbour	5	coal	15	1
3	8	27	Texusgulf-NPR	5	coal	15	1
4	8	27	Texusgulf-NPR	5	coal	15	1
5	8	32	Long Harbour	-	3L coal/1.5L LHS	15	1
6	8	32	Long Harbour	-	3L coal/1.5L LHS	15	1
7	8	32	Texusgulf-NPR	-	3L coal/1.5L NPR	15	1
8	8	32	Texusgulf-NPR	-	3L coal/1.5L NPR	15	1
9	8	47	-	-	-	-	1
10	8	47	-	-	-	-	1

Table 2: PERD Test Pile No. 5, Effluent Chemistry Data - 19

	June 11	June 29	August 6
pH	7	2.3	3.4
Conductivity (uhmos/cm)	20700	8510	2700
Turbidity (NTU)	5.9	3.4	0.56
Colour (TCU)	0	15	15
SO4 (mg/L)	11199	8715	1390
Cl- (mg/L)	463	2.3	21.8
ortho-phosphorus	<0.01	<0.01	0.05
nitrate-nitrite N (mg/L)	<0.01	<0.01	0.51
ammonia N (mg/L)	<0.01	<0.01	27.8
Al (mg/L)	-	246	43.2
Cu (mg/L)	0.02	6.81	0.33
Fe (mg/L)	0.4	1360	6.72
Mn (mg/L)	7.9	32.6	12
Zn (mg/L)	3.79	12.3	2.69

Schematic 1: Set-up of Laboratory Column Experiment




CONCEPTUAL PLACEMENT OF NPR
Schematic 2
Water Collection
Leachate Piping and Gravel Cover
Liner
Leak Detection Layer
100mm PVC Pipe
Water Collection
NPR
Precipitation Layer
5 Metres (approx.)

BU0591S.WK0 (7.18) XRAL 18-Jun-91 ug/g [ppm]

SAMPLE DATE		30-May-91
SAMPLE VOLUME		
ASSAYERS CODE		2708
SAMPLING LOCATION		BUCHANS Long Harbour Sand
Processing code		SS
** F I E L D **		
Temp. (C)		
pH		
Cond. (umhos/cm)		
Eh (mV)		
Acidity (mg/l)		
Alkalinity (mg/l)		
Ferric (Fe3+)		
Ferrous (Fe2+)		
** L A B **		
Temp. (C)		
pH		
Cond. (umhos/cm)		
Eh (mV)		
Acidity (mg/l)		
Alkalinity (mg/l)		
Ferric (Fe3+)		
Ferrous (Fe2+)		
ELEMENTS	Ag	< 2
	Al	7100
	As	< 10
	B	16
	Ba	50
	Be	
	Bi	
	C	
	Ca	320000
	Cd	6
	Ce	37
	Co	< 2
	Cr	48
	Cu	58
	Fe	8190
	Hg	
	K	776
	La	
	Mg	2580
	Mn	200
	Mo	< 2
	Na	4850
	Nb	
	Ni	10
	P	150000
	Pb	23
	S	6300
	Sb	
	Se	< 100
	Si	190
	Sn	< 10
	Sr	890
	Te	
	Th	< 2
	Ti	
	U	< 100
	V	
	W	
	Y	
	Zn	95
	Zr	

DN0792S1.WKQ [8.11] EPL 17-09-92 solids

SAMPLE DATE		16-Jul-92
SAMPLE VOLUME		
ASSAYERS CODE		4084
SAMPLING LOCATION		DENISON New waste phosphate sand
Processing code		SS
** F I E L D **		
Temp. (C)		
pH		
Cond. (umhos/cm)		
Eh (mV)		
Acidity (mg/l)		
Alkalinity (mg/l)		
Ferric (Fe3+)		
Ferrous (Fe2+)		
** L A B **		
Temp. (C)		
pH		
Cond. (umhos/cm)		
Eh (mV)		
Acidity (mg/l)		
Alkalinity (mg/l)		
Ferric (Fe3+)		
Ferrous (Fe2+)		
ELEMENTS	Ag	< 2
	Al	2500
	As	< 10
	B	331
	Ba	32
	Be	< 1
	Bi	< 8
	C	
	Ca	313000
	Cd	2
	Ce	
	Co	< 1
	Cr	49
	Cu	5
	Fe	5230
	Hg	
	K	1460
	La	
	Mg	2750
	Mn	21
	Mo	< 2
	Na	5000
	Nb	
	Ni	10
	P	71300
	Pb	< 3
	S	8070
	Sb	
	Se	< 10
	Si	120
	Sn	< 8
	Sr	2060
	Te	
	Th	
	Ti	42
	U	< 5
	V	16
	W	
	Y	
	Zn	76
	Zr	

APPENDIX 3

THE PHITO COVER

BACKGROUND AND LABORATORY DATA

DENISON FIELD EXPERIMENT

INCO FIELD EXPERIMENT

PROGRESS REPORT

THE PHITO COVER

Phosphate-Heterotroph Inhibition of Tailings Oxidation

May 19, 1993

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LIST OF TABLES

PROGRESS REPORT: THE PHITO COVER

Phosphate-Heterotroph Inhibition of Tailings Oxidation

May 19, 1993

1.0 INTRODUCTION

What is to be achieved and demonstrated?

The objective is to demonstrate that, in tailings, phosphate rock particles and an appropriate organic carbon source, supplied along with a vegetation cover, provides:

a) secondary mineral formation on and within the tailings particle matrix, which will reduce the permeability of the tailings and reduce access of oxygen to the pyrite particles.

b) oxygen depletion, due to growth of heterotrophic microbial communities which should reduce the activity of oxidizing bacteria such as *Thiobacillus*.

The PHITO cover will operate in the long-term as a terrestrial ecosystem, where plants and phosphate rock interact to favour the growth of oxygen-consuming, heterotrophic bacteria. With the proposed operation of the PHITO cover, several processes will work concurrently inside the inhibitory tailings cover.

a) Geochemical interactions between tailings and phosphate rock

b) Effects of secondary mineralization on vadose zone behaviour

c) Vegetation cover development

d) Microbial community development

The different components of the overall research program to develop the PHITO cover were outlined in a submission to the MEND Prevention and Control Committee. The submission is included with this package (see first section).

The literature on the subject of phosphate rock use as an amendment to coal wastes to inhibit or reduce acid generation was reviewed in a report detailing the first phase of the NRC/Boojum project. This submission, to the NRC, presented data from ongoing experiments with waste rock, and the first observations on SEM. These micrographs showed how and where secondary mineral precipitation is expected. This submission is also included in this package (see preceeding report). This report preceded the tailings test plot development, and was outlined in the project proposal as Phase 1 ($15,000).

The work presented in this report addresses the design of the test plot on relatively fresh Inco tailings.

2.0 PHITO COVER

2.1 Development of Measurement Methodology

While measurement of the acidity or alkalinity of a liquid is a standardized procedure (ASTM 2310, 2320), methods for measuring acidity in the tailings have to be derived from methods used for soil and sediments.

It stands to reason that, if a tailings cover is to be developed which reduces the acid generated, a method to quantify the generated acid be available.

Acid generation is generally measured as the Acid generation Potential (AP), but this measure would not change if acid generation were inhibited. Inhibition would prevent the AP, defined below, from being realized.

Acid Producing Potential Measurement

AP = S% * 31.25 Kg CaCO3 /tonne (S%, total S in sample)

NP = Neutralization Potential (titrate fine ground slurry to pH 3.5)

NAP = Net Acid-producing Potential

NAP = AP - NP

For the monitoring of the test plot, we need to have a measure of the acid produced, or not produced, due to the treatment applied to the plot. We therefore tested the method given in S.E. Allen, "Chemical Analysis of Ecological Materials" as it might be used for tailings. A brief review of acidity and the method is given in Section 2.2.

2.2 Method: Acidity of Solids

The method employed by Boojum Research Ltd., and described below, has been devised to quantify the amount of acidity present in a volume of tailings. This parameter should not be confused with the gross or net acid generating or consuming potential of tailings, soils or sediments.

The acidity of a solid is its quantitative capacity to react with a strong base to a designated pH, e.g. pH 8.3. Acidity is a measure of the aggregate property of the solid and can be interpreted in terms of specific substances only when the chemical composition of the sample is well known. Strong mineral acids, weak acids such as carbonic and acetic, and hydrolysing salts such as iron or aluminum sulphates may contribute to the acidity (Standard Methods, 1989).

2.3 General Discussion

a) Principle: Hydrogen ions, present in a sample as a result of dissociation or hydrolysis of solutes, react with additions of standard alkali. Acidity thus depends on the end-point pH used.

Because accurate identification of inflection points may be difficult or impossible in buffered or complex mixtures, the titration in such cases is carried to an arbitrary end-point pH based on practical considerations.

b) End Points: Ideally, the end point of the acidity titration should correspond to the stoichiometric equivalence point for neutralization of the acids present. In uncontaminated water, for instance, pH 8.3 represents the point where carbonic acid has been neutralized to bicarbonate. Because tailings contain complex, buffered solutions, a fixed end-point of 8.3 is used for standard acidity determinations, via potentiometric titration where the simple carbonate equilibria cannot be assumed.

c) Interferences: Dissolved gases contributing to acidity or alkalinity, such as CO_2, H_2S, or ammonia, may be lost or gained during sampling, storage or titration. Therefore, samples should be titrated as soon as possible, avoiding exposure to atmosphere, or heat.

d) The method of tracing pore water for soils: Weigh 10 g (tailings or soil) or 25 g (peat) of sample into a Pyrex beaker. Add 250 mL of distilled water and stir for one hour on a magnetic stirrer. Pour 200 mL of the supernatant liquid through No. 44 Whatman filter paper into a clean dry beaker, collect the filtrate (Filtrate 1), determine chloride base concentration in Filtrate 1, and set filtrate aside.

Rinse the filter paper with a further 50 mL of Filtrate 1 and 10 mL 10% NH_4Cl (or NaCl) solution into new beaker. Collect Filtrate 2 and test for chloride. If chloride is no more than 1 mg/L higher than the base chloride concentration, the test is complete. Otherwise, add 50 mL more filtrate to leach the sample and collect another sample of Filtrate 2, then test for chloride. Repeat addition of Filtrate 1, and collection and testing of Filtrate 2 until no chloride is detected. Pool Filtrate 1 and Filtrate 2

volumes and measure the total volume. Sample 10 mL from the Filtrate and perform acidity titration to pH 8.3 (after G. S. Allen,"Chemical Analysis of Ecological Materials").

2.4 Measurements of Tailings Acidity

In order to develop a method for tailings acidity measurement, the following considerations should be examined:

1. Whether the ratio of extractant and soil will affect the acidity value.
2. Whether the mixing time of slurry will affect the acidity value.
3. The number of filtrations which should be done in order to guarantee all cations in pore water are removed and measured.

To answer these questions, the experiment was divided into several groups. An extract of tailings was prepared by mixing 10 g of tailings with 250 mL extractant or other ratios, stirring the slurry for one hour, then filtering the slurry solution. The filtrate was titrated. Acidity of each tailing sample was tested at two different soil/water ratios (20/30 and 10/50), different mixing times (one hour or several days) and with or without a tracer (NaCl solution). The tracer (NaCl solution) was added during the filtration, then the slurry was further washed and filtered, until there was no Cl^- ion tested in the filtrate. Using a tracer assures that all the pore water in the tailings has been washed from the sample. Then 10 mL of filtrate was titrated with 0.01 N NaOH solution to pH 8.3. Tailings acidity is calculated as:

filtrate acidity ($CaCO_3$ mg/L) = mL(NaOH)*50
tailings acidity ($CaCO_3$: g/g) = filtrate acidity * mL (total filtrate) / g (tailing)

Two kinds of tailings samples were chosen for the experiment. Tailings from INCO. Several different tailings batches were tested: (A) was low acidity. (B) tailings were of high acidity. In the measurement all the tailings were freshly collected without drying and disturbing any physical characteristics. The test results are listed in Table 1a.

The results show that, for high acidity tailings, the soil/water ratio, mixing time and tracer do not affect the final acidity value significantly. For the low acidity tailings, the results are variable and may be related to the heterogeneity of the tailings material. Therefore, if the acidities are around 100 $CaCO_3$ equivalents, differences in 100 should not be interpreted as relevant results.

TABLE 1a: Tailings Experiment - Methods

Sample Name	soil/water	vib.time hour	NaCl	soln.vol. mL	Acidity soln.(mg/L)	Acidity soil(ug/g)
Inco (A)	20/30	66	-	76	4.6	17.48
	20/30	66	+	118	15.6	92.04
	20/30	1	-	42	153.7	322.77
	20/30	1	+	171	12.1	103.455
	10/50	66	-	79	91.4	722.06
	10/50	66	+	114	10.8	123.12
	10/50	1	-	46	40.2	184.92
	10/50	1	+	145	9.6	139.2
Inco (B)	20/30	66	+	109	895.2	4878.84
	20/30	66	-	66	1633	5388.9
	20/30	1	+	143	773.3	5529.095
	20/30	1	-	102	972.9	4961.79
	10/50	66	+	141	415.4	5857.14
	10/50	66	-	68	807.4	5490.32
	10/50	1	+	145	397.1	5757.95
	10/50	1	-	97	547.4	5309.78

To determine the tailings acidity, the following procedure was adapted:

Ten (10) grams of tailings sample are mixed with 50 mL distilled water, shake or stir the mixture for one hour, then filter the supernatant through a vacuum filter. Use a small amount of distilled water to wash the remaining tailings twice, and then transfer the solids onto the filter in the funnel. Filter, and measure the total volume of the filtrate. Take 10 mL of the filtrate and titrate its acidity. Calculate the tailings acidity according to the equations:

$$\text{Acidity (: g } CACO_3 \text{ equiv./ g tailings)} = \frac{(\text{mL NaOH/mL sample}) * (\text{N NaOH} * 50{,}000) * \text{mL Total Filtrate})}{(\text{g of fresh tailings})}$$

where: mL NaOH = the volume of NaOH necessary to bring sample to pH 8.3.

where: N is the normality of the NaOH

where: mL of total Filtrate = total volume of all filtrates collected.

No general statement can be made about precision because of the great variation in sample characteristics. The precision of the titration is likely to be much greater than the uncertainties involved in sampling and sample handling before analysis.

Materials and reagents:

Metrohm Titrino autotitrator; 0.01 or 0.1 N NaOH. Scale accurate +/- 0.01 mL.

Beakers, 300 mL volume; magnetic stirrer; Whatman No. 44 filter papers; plastic Funnels; 10% NH_4Cl or NaCl solution, distilled water.

3.0 PHOSPHATE ROCK DOSAGES FOR INCO/DENISON TAILINGS

Determination of the phosphate application rate is being addressed by a lab experiment and a series of calculations. The purpose of the first experiment was to test the practical acid-reducing ability of different types phosphate sand, determined by the reactions with different samples of tailings. Based on the experimental results, it will be possible to choose a reasonable dosage of phosphate sand for application in the field. The results of this experiment are described in Section 3.1.

Based on the experimental results, calculations were performed concerning the phosphate requirement of each tailings type. The results of these calculations are described in Section 3.2.

3.1 Phosphate Rock Dosage Experiment

The field testing will be carried out with coarse or gravel phosphate supplied by Texasgulf. Lab testing, however, utilized four types of phosphate sands. They primarily vary according to particle size and phosphate content (Table 1b). The coarse phosphate rock has a highest density, but the lowest phosphorus content. Otherwise, the major chemical components of all the phosphate rock types are similar. Code 132 sand has been calcined which transforms $CaCO_3$ into CaO.

The alkalinities of the phosphate sands were determined using the same method as was used for tailings acidity, except that alkalinity titrations using H_2SO_4 were performed. Alkalinities were measured by titrating the extract from the slurry of 10 g phosphate rock with 50 mL distilled water. The titration curves of the four types phosphate sands are shown in Figure 1a and 1b (note different scales). It can be seen that Code 31 phosphate rock released most alkalinity to the slurry within one hour of stirring, while Code 132 phosphate rock slurry reached the highest pH, as would be expected from calcined material.

Five samples of Inco tailings and one Denison tailings sample were used in the experiment. Their acidities and physical characteristics are listed in Table 2. Tailings samples A and D were relatively fresh, and had lower acidities, conductivities and higher pH. However, the slurries of these two samples required a greater number of rinses to raise the pH. The rising pH range was determined, to assess the quantity of rain water which would be required to neutralize or raise the pH in the tailings.

Tailings samples B and C were more oxidized. The slurries contained higher acidities and conductivities (likely due to ferrous ion concentrations). These slurries did not require many rinses to raise the pH, as the acidity was easily liberated from the tailings.

Each of the four types of phosphate rock were applied to each type of tailings. In addition, two dosages of phosphate rock were applied to each tailings type. The low dosage was decided upon by after economic evaluation (allowing for replacement of limestone used to establish a regular vegetation cover on the tailings given at $2500/ha). Using the cost of phosphate rock per tonne of $Can 81.00 (shipping and material costs, as quoted by Texasgulf). This would result in a cost of material of $0.08 /kg. If we plan the dosage to be the same price as lime, then $ 2,500 are available for 10,000 m^2, which results in an application ratio of phosphate rock to tailings of 3 kg/m^2. Assuming that phosphate rock is worked into the tailings to a depth of 20 cm, then the ratio of phosphate sand to tailings is 3 kg/m^2 * 10^5 cm^3, or 3 g/ 200 mL.

TABLE 1b: Phosphate Sand Properties

	coarse	code 30	code 31	code 132
particle size	mesh 6-14	mesh 65-100		finest
Density	1.74	1.5375	1.135	1.61
Alkalinity	1,230	1,350	20,950	9,700
mg/L(CaCO3)	6,200	2,100	29,905	11,860
average	3,715	1,725	25,428	10,780
ICP Al mg/L	2,500	2,040	2,050	2,440
Ca mg/L	313,000	331,000	311,000	361,000
Fe mg/L	5,230	3,200	3,260	4,690
P mg/L	71,300	128,000	121,000	139,000
S mg/L	8,070	10,300	10,600	12,100

TABLE 2: INCO and Denison Tailings - Physical Properties

Tailings	A	B	C	D	E	Denison
Acidity (mg/L)	422.59	5674	6932	638	18.05	406
Density (g/mL)	1.11	1.28	1	1.415	1.205	1.63
Cond. (20g/100mL slurry)	500	1600	1900	400	120	2200
Water passed (mL)	20	5	30	40	0	92
pH rising range	3.75-5.20	4.23-5.34	3.89-5.40	3.77-5.01	6.24	3.34-5.06
Initial Wt. (g)	20.81	47.5	36.5	39.5	36.5	63.3
Dry Wt. (g)	20.05	45.57	33.67	39.01	31.53	44.4
Moisture (%)	3.65	4.06	7.75	1.24	13.62	29.86

Fig. 1a: Texasgulf Phosphate Alkalinity
1g/50mL stir 1 hour

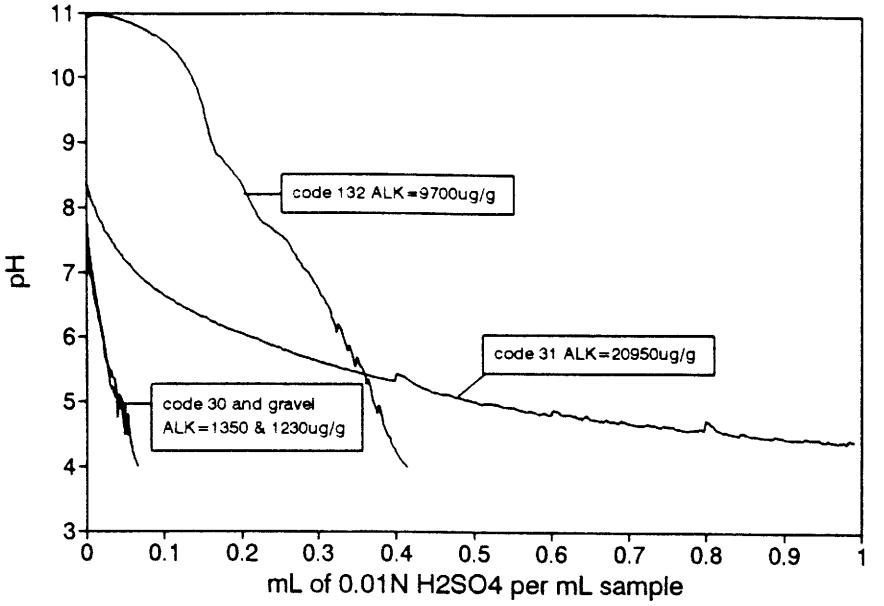
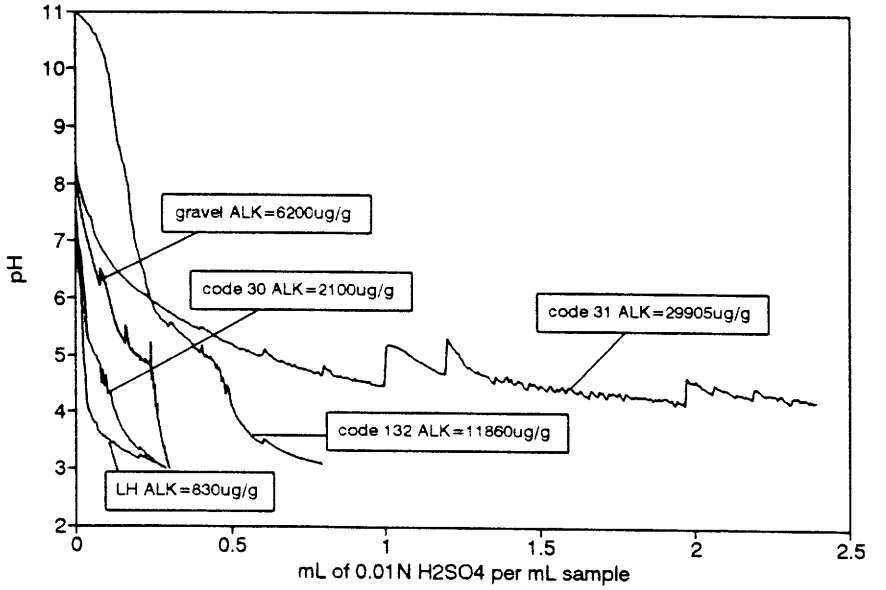


Fig. 1b: Phosphate Alkalinity
1g/50mL stir 1 hour



The second dosage was set, based on the acidity of the tailings and the alkalinity of phosphate sand. The acidity of 200 mL of tailings was calculated, and then the amount of phosphate sand required to provide the equivalent alkalinity (based on 1 hour slurry) was calculated.

In the case of Inco tailings B and C (high acidity), this approach could not be employed, since coarse phosphate rock and Code 30 release relatively little alkalinity in 1 hour, and the amount of phosphate rock required would far outweigh the amount of tailings. Therefore, a phosphate rock:tailings volume ratio of 1:1 for Inco tailings B, and 1:2 for tailings C were chosen. Tailings sample E was totally fresh, non-oxidized, and its acidity was very low. Since the Denison tailings (Stanrock) sample was wet, and very plastic, working of the phosphate rock into the Denison tailings was very difficult. Therefore, only a low dosage was applied to the surface of the tailings sample. For the remaining tailings types, phosphate rock was worked in. All dosages of phosphate rock are listed in Table 3.

The experiment was set up in planting trays. In each treatment, phosphate rock and tailings were placed into four planting slots. Each slot volume was 50 mL. To simulate rain and assist the reaction with phosphate rock, a litre of tap water was sprayed on the experiments every day.

Altogether, 8300 mL (9960 g) of tailings were used to set up the experiment. Therefore, after 10 days, approximately 10 mL of water had passed through each 10 g of tailings. Then acidity of each treatment was measured after 11 days. The results are given in Table 4, and Figures 2 through 6.

Compared to the controls, most tailings sample acidities decreased, with the exception of the Inco B and Denison tailings. In all tailings samples, the low dosages of Code 30 and 31 were very effective. The high dosage phosphate rock application reduced most acidities to less than 50 mg/L, except for tailings samples A and C, where coarse phosphate rock was applied.

These experimental results can be used to rank the phosphate rock types based on a range of released alkalinities to the different tailings acidities. A calculation which permits comparison of the acidity reducing ability of each phosphate rock type can be introduced:

$$\text{Acid Reducing Ability, ARA} = \frac{(\text{Final Tailing Acidity} - \text{Original acidity}) * (\text{tailing wt.})}{\text{sand wt.}}$$

This ARA calculation has been made for each type phosphate sand in each treatment. Results are plotted in Figure 7.

Negative ARA values indicate that acidities were reduced. It is evident, that Code 31 phosphate rock has the highest ARA value. The average ARA value of Code 31 in 9 tailings treatments, not including tailings C, is about -98,000 ：g acidity/g phosphate rock. Based on ARA calculations, then, Code 31 sand appears to be the best type of phosphate rock for rapidly neutralizing acidity present in tailings.

Although Code 31 is not the material which is available for the test plot, an evaluation of cover costs might be useful, with respect to the use of this material as both a fertilizer and acidity neutralizer. The experiment will continue to run, as these are the results of obtained only after 11 days, and the effect of the material is expected to last longer. It can be concluded, that the low application rate of 3kg/m^2 will be effective.

TABLE 3: Phosphate to Tailings Ratio

PS/Tailings	Coarse	code 30	code 31	code 132
A (low)	2.5g/200mL	2.9g/200mL	2.5g/200mL	3g/200mL
A (high)	23/200	49/200	6/200	8/200
B (low)	2.5g/200mL	2.9g/200mL	2.5g/200mL	3g/200mL
B (high)	150/150	150/150	45/200	79/150
C (low)	2.5g/200mL	2.9g/200mL	2.5g/200mL	3g/200mL
C (high)	75/150	75/150	45/200	79/150
D (low)	2.5g/200mL	2.9g/200mL	2.5g/200mL	3g/200mL
D (high)	34/200	74/200	10/200	12/200
E (low)	2.5g/200mL	2.9g/200mL	2.5g/200mL	3g/200mL
Den (low)	2.5g/200mL	2.9g/200mL	2.5g/200mL	3g/200mL

* PS/tailings volume ratio used in the high ratio treatment

TABLE 4: Changes in pH and Acidity in Tailings Over 11 Days (Apr 22 to May 3, 1993)

	Coarse		code 30		code 31		code 132	
	pH	Acid.ug/g	pH	Acid.ug/g	pH	acid.ug/g	pH	acid.ug/g
A (control)	5.49	325.36						
A (low)	5.38	151.94	6.34	103.84	5.46	83.49	3.52	801.92
A (high)	5.74	77.35	6.10	40.85	6.21	42.72	5.61	91.16
B (control)	4.06	12843.07						
B (low)	5.22	7298.58	5.05	7366.08	4.87	6393.54	4.34	13247.59
B (high)	7.88	19.14	7.17	22.77	7.13	35.31	8.08	11.66
C (control)	4.28	1867.45						
C (low)	4.26	4272.85	4.74	3106.84	4.79	2766.06	4.55	3254.73
C (high)	6.83	119.88	7.02	49.28	7.18	35.52	8.02	9.20
D (control)	5.22	206.85						
D (low)	5.36	386.28	5.85	197.40	6.56	127.00	5.46	231.42
D (high)	7.15	38.25	7.51	18.92	7.12	27.72	7.13	26.00
E (control)	7.57	10.35						
E (low)	7.54	9.90	7.64	9.12	7.76	8.36	7.54	12.30
Den (control)	3.39	869.12						
Den (low)	3.30	1224.02	6.24	48.45	6.45	77.49	5.97	62.22

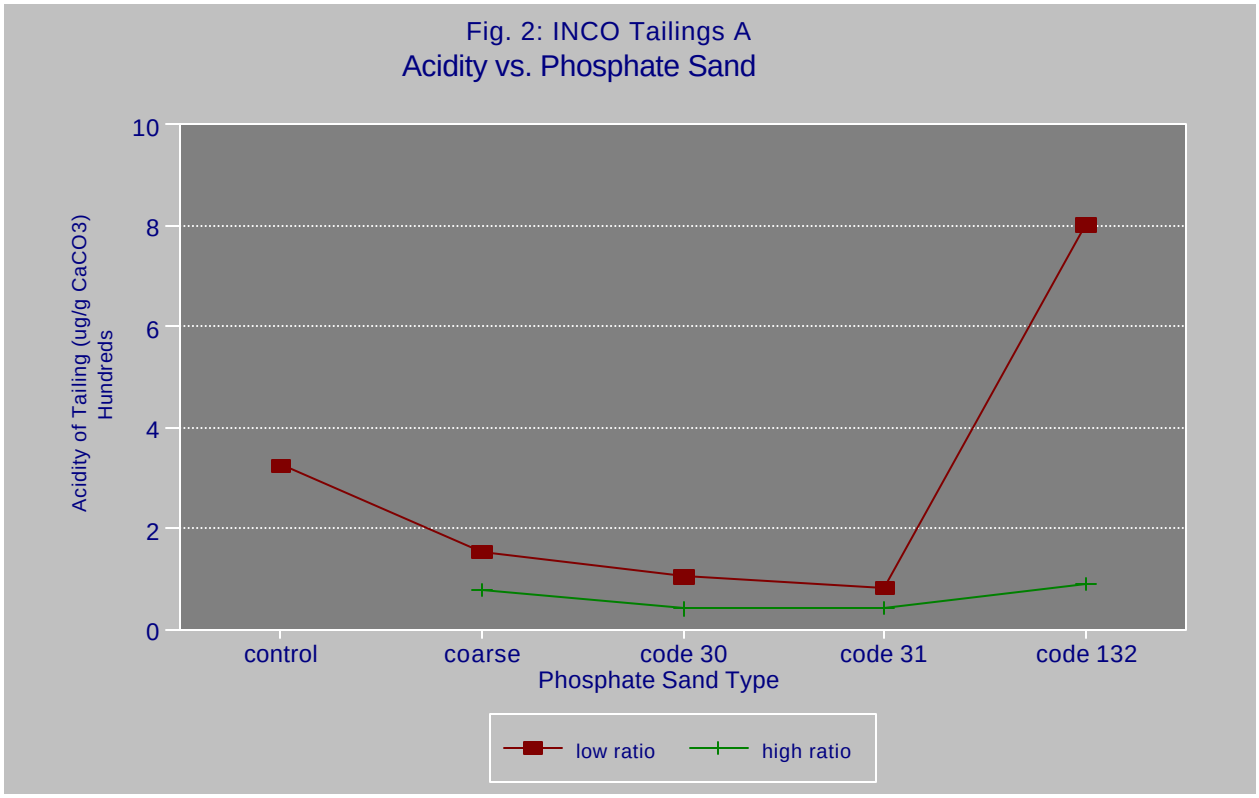


Fig. 2: INCO Tailings A
Acidity vs. Phosphate Sand
Acidity of Tailing (ug/g CaCO3)
Hundreds
10
8
6
4
2
0
control
coarse
code 30
code 31
code 132
Phosphate Sand Type
low ratio
high ratio

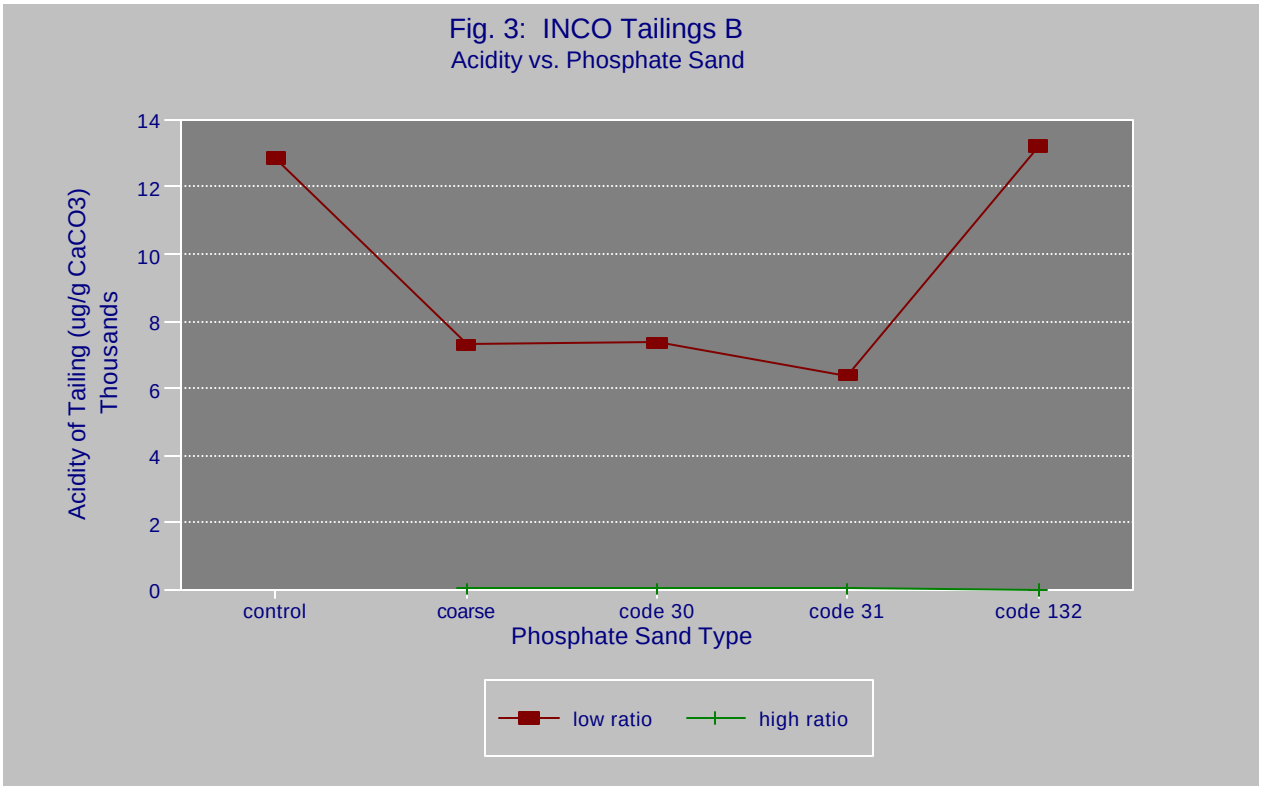


Fig. 3: INCO Tailings B
Acidity vs. Phosphate Sand
Acidity of Tailing (ug/g CaCO3)
Thousands
14
12
10
8
6
4
2
0
control
coarse
code 30
code 31
code 132
Phosphate Sand Type
low ratio
high ratio

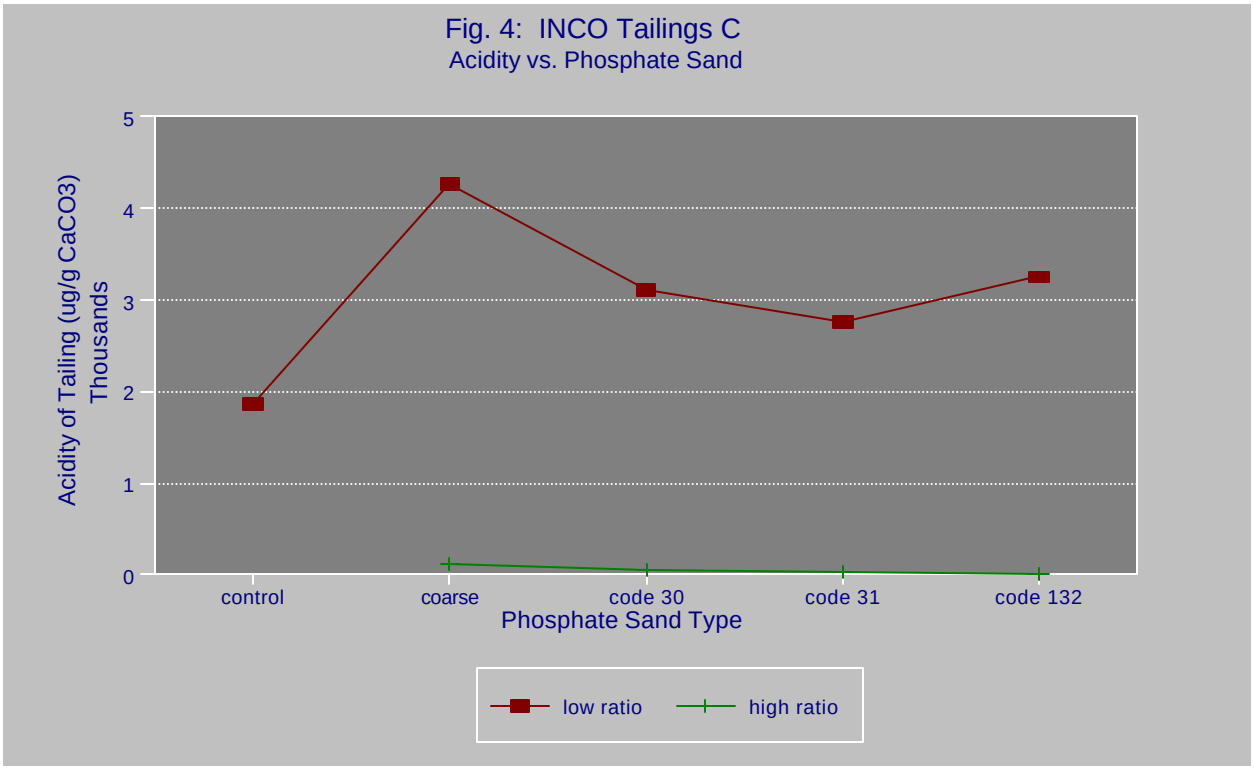


Fig. 4: INCO Tailings C
Acidity vs. Phosphate Sand
Acidity of Tailing (ug/g CaCO3)
Thousands
5
4
3
2
1
0
control
coarse
code 30
code 31
code 132
Phosphate Sand Type
low ratio
high ratio

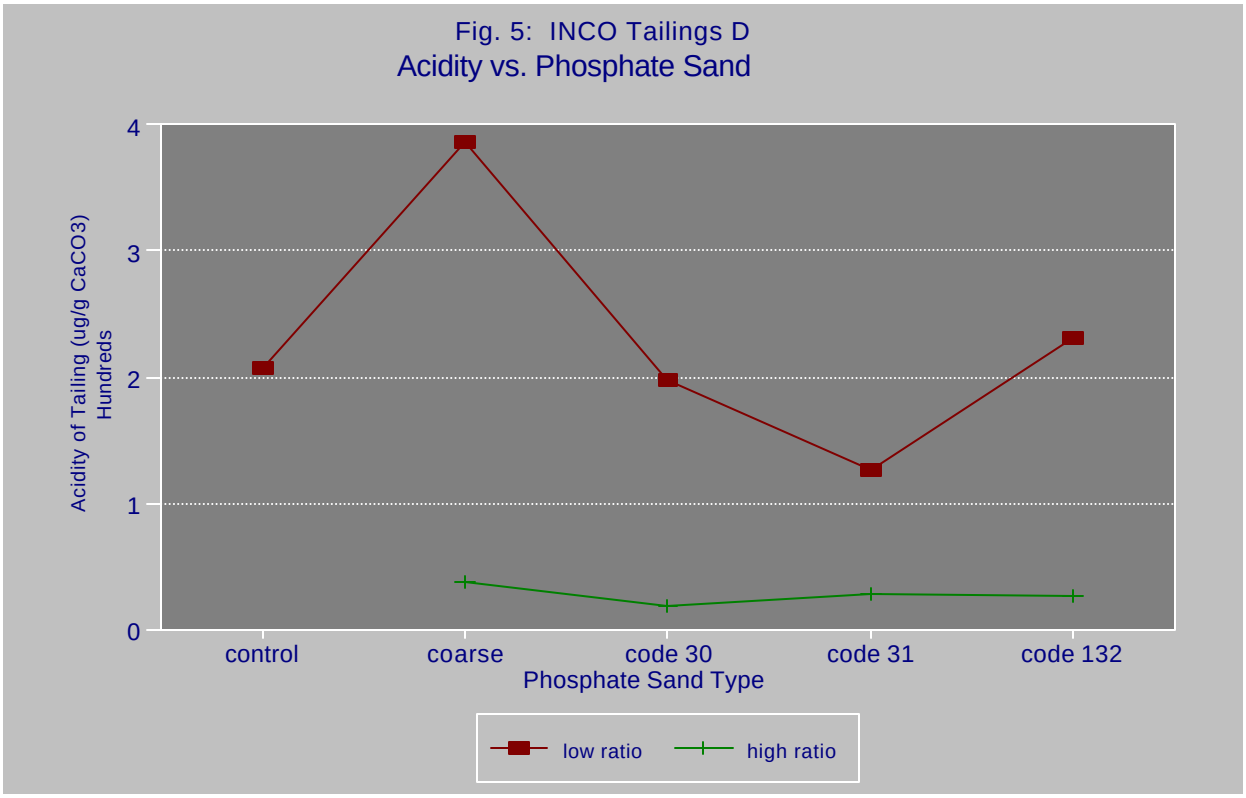


Fig. 5: INCO Tailings D
Acidity vs. Phosphate Sand
Acidity of Tailing (ug/g CaCO3)
Hundreds
4
3
2
1
0
control
coarse
code 30
code 31
code 132
Phosphate Sand Type
low ratio
high ratio

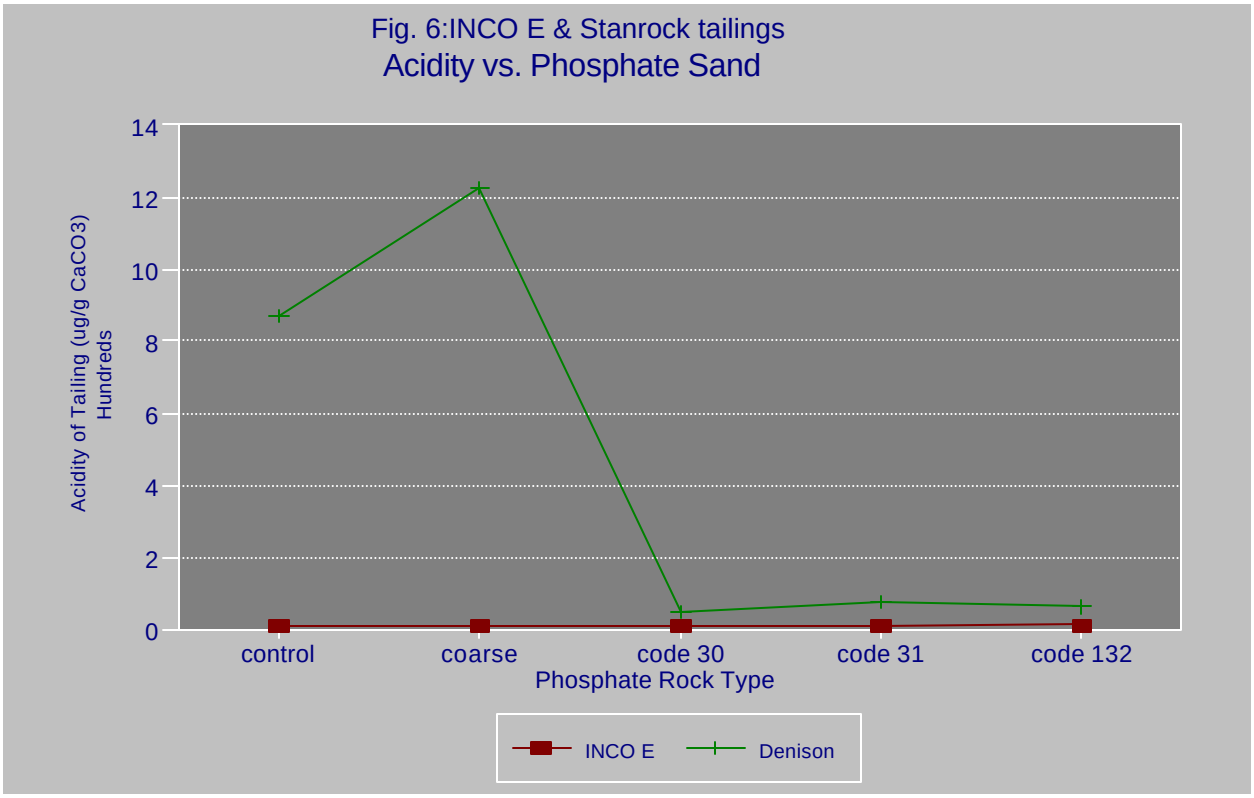


Fig. 6:INCO E & Stanrock tailings
Acidity vs. Phosphate Sand
Acidity of Tailing (ug/g CaCO3)
Hundreds
14
12
10
8
6
4
2
0
control
coarse
code 30
code 31
code 132
Phosphate Rock Type
INCO E
Denison

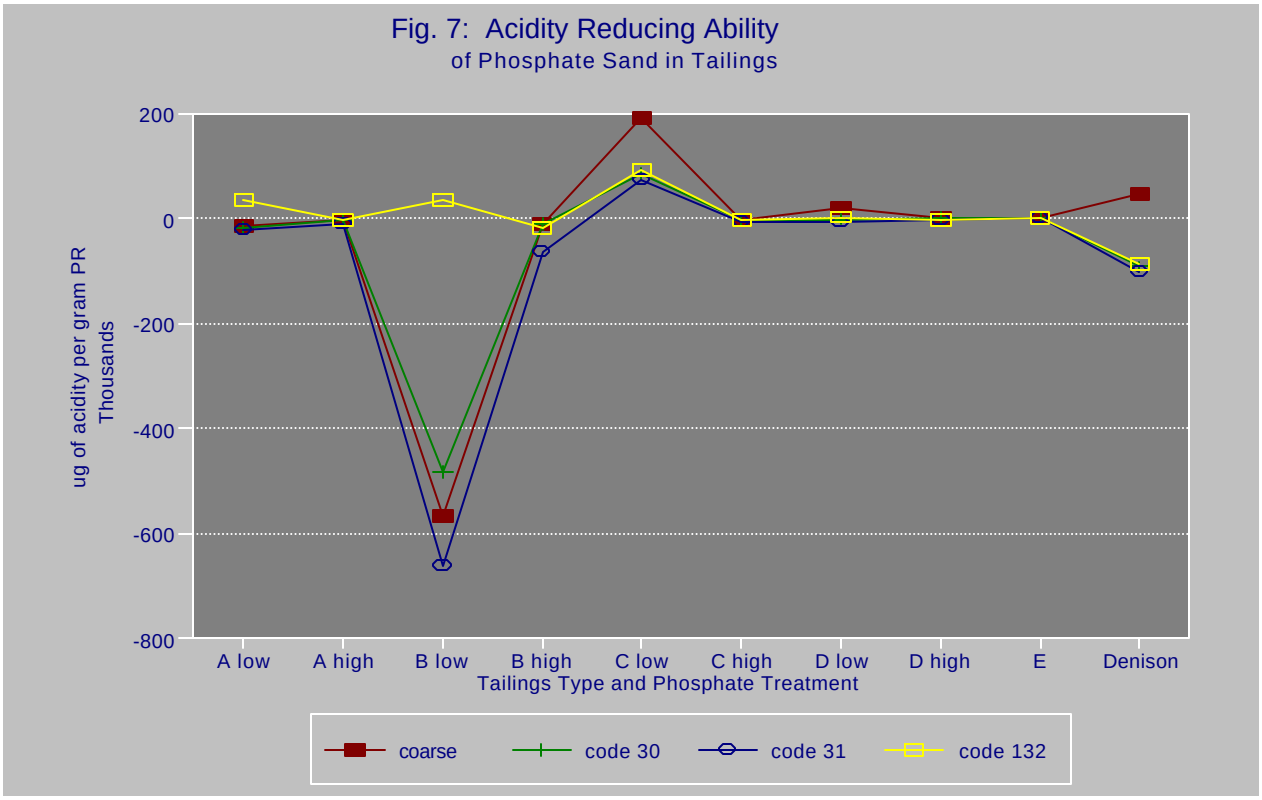


Fig. 7: Acidity Reducing Ability
of Phosphate Sand in Tailings
ug of acidity per gram PR
Thousands
200
0
-200
-400
-600
-800
A low
A high
B low
B high
C low
C high
D low
D high
E
Denison
Tailings Type and Phosphate Treatment
coarse
code 30
code 31
code 132

3.2 Phosphate Rock Requirements

Based on the first experiment results, calculations concerning phosphate rock requirements were performed. Each tailings' acidity in a 1 m^2 area 20 cm deep was calculated. The amount of code 31 phosphate sand and the coarse sand needed for this 1 m^2 tailings area was calculated using the appropriate ARA value. The results are listed in Table 5. Using these ARA values, the application rates for tailings samples B and C would be around 24 kg/m^2, but for all other types (A, D, E and Denison tailings) the proposed rate of 3 kg/m^2 is reasonable.

TABLE 5: Phosphate Sand Requirements Calculated from Lab Experimental

g/m2 (PS)	A	B	C	D	E	Denison
Code 30	960	14871	14193	1848	45	1355
Coarse	1593	24658	23535	3065	74	2247

Another approach to calculating the phosphate rock dosage was calculated using the chemical analysis of major elements in ore provided by the Inco Clarabelle Mill laboratory. The average percent sulphur in the concentrate and tailings is 5.78 %. The oxidation process of pyrrhotite or pyrite can be summarized as follows:

$$15\ O_2 + 14\ H_2O + 4\ FeS_2 = 8\ SO_4^{-2} + 4\ Fe(OH)_3 + 16\ H^+$$

$$9\ O_2 + 10\ H_2O + 4\ FeS = 4\ SO_4^{-2} + 4\ Fe(OH)_3 + 8\ H^+ \quad \text{or}$$

$$Fe_{1-x}S + 3(3-x)/2\ O_2 = (1-x)Fe(OH)_3 + SO_4^{-2} + 2H^+$$

In the above reaction equations, the molar ratio between S and H^+ is 1:2. According to this ratio, if all the S in the tailings is sulphide, and it is all oxidized to sulphate, then the tailings total capacity to generate acidity is 180.63 mg/g equiv. $CaCO_3$. In the long- term, application rates of 400 to 600 kg/m^2 would be required if neutralization of the AP of the tailings were supplied by phosphate, and assuming that acid generation would proceed to complete exhaustion of S.

Clearly, such an application rate is not required if the acid generation is inhibited with the proposed PHITO cover.

4.0 GERMINATION OF GRASS SEEDS ON INCO/DENISON TAILINGS

From the work carried out to date with fresh tailings and vegetation establishment, three steps are required:

1) introduction of phosphate rock into the top 20 cm of the tailings.

2) addition of organic matter into the proposed root zone, in this case, horse manure.

3) seeding of the surface.

A laboratory experiment was set up to determine whether seeds would germinate, and seedlings would establish on tailings samples used in the above tests. These tailings should be physically and chemical similar to those which will underlie phosphate rock field experiments. The effects of horse manure supplied by Inco (Sudbury) and phosphate rock (Code 31) on germination were assessed.

The following treatments were set up:

Ref. No.	Tailings Type and Treatment
1)	Inco tailings A
2)	Inco tailings B (weathered)
3)	Inco tailings C (weathered)
4)	Inco tailings D
5)	Inco tailings E (fresh)
6)	Denison tailings (Stanrock)
7)-12)	As for 1) to 6) w/ addition of phosphate rock (rate equivalent to 3 kg/m^2)
13)-18)	As for 1) to 6) w/ addition of 3 year old horse manure (rate of 31 g/L)
19)-24)	As for 13)-18) with addition of phosphate rock at 3 kg/m^2
25)-36)	As for 13)-24) with the addition of manure at the rate of 200 g/L.

The phosphate rock application rate was the same rate used in the 'economical rate calculations' described above, and which was based on lime costs of approximately $2400 /ha. The horse manure application rates were calculated in the following manner. The amount of fertilizer should be able to provide a year's nitrogen supply to a healthy plant cover. Since experiments at Selbaie had already used 138 kg N/ha, and this application sustained a healthy plant cover over one year, it was used again for these experiments.

Using a figure of 1 % N in dry manure, and a percent dry weight of 44.5 (determined in the lab), a rate of 31 tonnes fresh weight of manure per ha, or 31 g/L tailings was employed. A much higher rate (200 tonne /ha or 200 g/L) was also tested. This would provide a larger quantity of organic matter which would stimulate heterotrophic bacterial activity and increase water holding capacity, in addition to providing neutralising capacity and fertilizer for the vegetation.

Three 50 mL 'pots' in seed trays were filled with the appropriate tailings mixture for each treatment. Each treatment was separated from the next to prevent cross contamination. The tailings were watered to saturation. For each treatment, 40 to 50 winter rye seeds and 0.3 g of grass-legume mixture were added. A sprinkling of the appropriate tailings type was then added to partially cover the seeds, simulating harrowing of the tailings surface. The trays were covered with a clear plastic sheet to reduce evaporatory water loss (compensating for low % R.H. in the lab) and placed under banks of fluorescent lights in the laboratory.

The first seeds germinated 40 h after setup. A few seeds (nearly all rye) had germinated in most tailings types, with the exception of Inco B tailings. After 60 h, it was apparent that the seedlings in Inco B and C tailings were suffering. Few had germinated and those which had, did not continue growing. At this time, there was little indication that the manure or phosphate rock were providing any beneficial effects.

Germination counts and seedling heights of germinated rye seedlings were recorded 112 h after sowing. The results are summarised in Tables 6 and 7. The number of germinated seedlings were clearly influenced by the type of tailings. In the treatment with tailings alone, no seeds germinated on Inco B tailings, and only 3 seeds germinated on Inco C tailings. A slightly greater number of seeds germinated on Inco A tailings (7), while many seeds germinated on Inco D (fresh Inco tailings) and the Denison tailings (14 to 25 seeds). Although seeds germinated on Inco A, C and D tailings with no phosphate rock or horse manure, the seedling growth was very poor; seedlings reached heights of no more than 0.19 cms. Seedlings on Denison tailings developed somewhat better, achieving heights of 0.8 cm. However, only those seedlings on fresh Inco tailings grew substantially, and were, on average, 5.3 cm tall after 112 hours following seeding.

It appears that germination frequencies and seedling development were at a maximum in the Inco fresh tailings (control) treatment, as the various applications of phosphate and horse manure did not improve seedling development. It should be pointed out that these treatments did not negatively affect germination or seedling development on fresh Inco tailings. For the remainder of tailings types, addition of phosphate rock improved germination frequencies,

TABLE 6: Effect of Phosphate Sand and Horse Manure on Numbers of Germinating Rye Seeds 112 Hours After Sowing

Tailings	Control	phos sand	low manure	low manure phos sand	high manure	high manure phos sand	Mean
INCO A	7	16	17	21	14	17	15
INCO B (weathered)	0	7	9	8	8	4	6
INCO C (weathered)	3	6	2	8	3	2	4
INCO D	18	15	21	18	10	12	16
INCO fresh	25	24	27	31	24	19	25
STANROCK	14	25	14	16	17	13	17
Mean	11	16	15	17	13	11	14

TABLE 7: Effect of Phosphate Sand and Horse Manure on Height of Seedlings on Taili 112 Hours After Sowing

Tailings	Control	phos sand	low manure	low manure phos sand	high manure	high manure phos sand	Mean
INCO A	0.19	0.5	0.25	0.91	1.1	2.2	0.86
INCO B (weathered)	0	0.23	0.17	0.19	0.11	0.23	0.16
INCO C (weathered)	0.1	0.1	0.1	0.13	0.13	0.2	0.13
INCO D	0.19	0.25	0.3	0.32	0.67	0.23	0.33
INCO fresh	5.3	4.7	3.8	4.8	5.5	5	4.85
STANROCK	0.8	6	1.6	4.8	4.8	2.7	2.55
Mean	1.1	1.96	1.04	1.86	2.06	1.73	1.48

especially in the case of Inco A and B, and Denison (Stanrock) tailings. However, despite higher germination frequencies, improved seedling development was evident only in the Denison (Stanrock) tailings with phosphate rock treatment.

The addition of the low dose horse manure had a similar effect on germination as phosphate rock. Improved germination frequencies were recorded for Inco A and B tailings. While manure did not improve germination when added to Stanrock tailings, compared to the control, it did somewhat promote development of seedlings.

The addition of phosphate rock and the low dose of manure increased seed germination frequencies, and slightly improved seedling development, in treatments with Inco A, B and C tailings, compared to control tailings treatments. However, the effect was not greater than in those treatments with phosphate or the low manure dosage treatments. Addition of a high dosage of manure alone, or the treatments with high manure dosage and phosphate rock did not further increase germination frequencies or improve seedling development beyond what the treatments with phosphate rock, low dosage manure or these two treatments combined in treatments with Inco A, B and C.

Overall, seeds can be expected to germinate on fresh Inco tailings with or without addition of phosphate rock or manure. Addition of phosphate rock or manure to older, weathered Inco tailings will not improve seedling development. Although not tested in the laboratory experiment, better germination and seedling development may be achieved on older tailings if the phosphate rock is allowed to weather and neutralize the pore water in the surface layer of tailings. Finally, seedling germination frequencies and seedling development were greatly enhanced by addition of phosphate rock and/or horse manure.

5.0 EXPERIMENTAL DESIGN FOR INCO FIELD EXPERIMENT

An experimental design for the field plot has been devised, based on economic (low dosage phosphate rock; Table 8). In Table 8, the high phosphate rock dosage is 30 kg/m^2. In this scenario, each plot can be 22 m x 22 m (484 m^2 in area). In all, the field experiment comprise nine treatments.

TABLE 8: INCO PHOSPHATE ROCK TEST PLOT

Phosphate Rock

50,000 kg of Coarse PR
0.2 m deep tailings zone
200 L per m2 of tailings

0.003 kg PR per 200 mL tailings, low application rate
0.015 kg PR per L tailings, low application rate
Therefore 3 kg PR per m2 of tailings, low application rate
16,667 m2 plot 129.1 m x ****** m plot
1.67 ha plot

0.03 kg PR per 200 mL tailings, high application rate
0.15 kg PR per L tailings, high application rate
Therefore 30 kg PR per m2 of tailings, high application rate
1,667 m2 plot 40.8 m x 40.8 m plot
0.17 ha plot

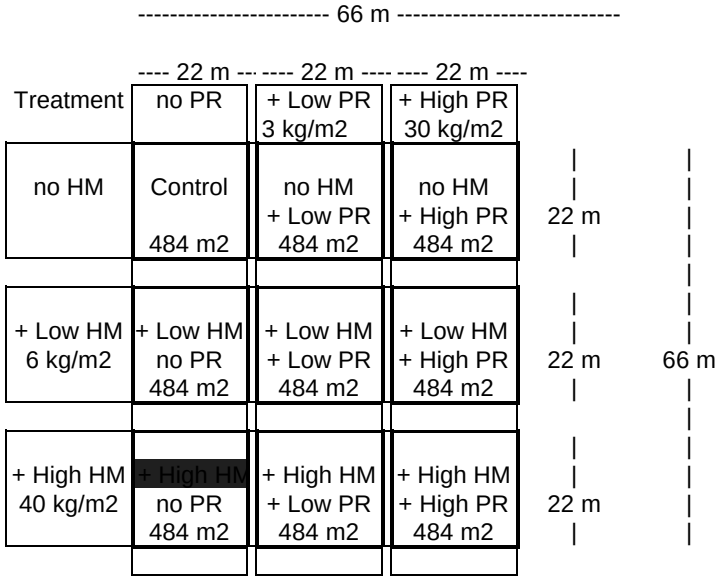
But, equal area plots! 1515 m2 of low application PR experimental area
1515 m2 of high application PR experimental area
39 m x 39 m plots
= Three times 22 m x 22 m plots

Horse Manure

31 g of HM per L of tailings, low application rate
200 g of HM per L of tailings, high application rate

Therefore

6.2 Kg HM per m2, low application rate
40 Kg HM per m2, high application rate



6.0 PRELIMINARY RESULTS

Base metal tailings, which had been used in early laboratory experiments, were used to test the long-term effect of phosphate rock mixture with peat. The mixing was carried out in a kiddy pool and pH was measured periodically in the first 45 days (Figure 8). In the figure, HP represents the high phosphate dosage without fertilizer; LP = the low phosphate dosage without fertilizer; and O = Osmocote only. The rate at which phosphate rock and fertilizer were applied was estimated to range from 4.5 kg/m^2 to 4.0 kg/m^2. This rate is equivalent to the high application rate discussed above, and shows that in the first 45 days, pH increased. The experimental set up was left sitting outdoors, and essentially ignored for one year.

In Table 10, acidity and pH are shown for fresh tailings covered with vegetation. These data were taken from the original experiments which lead to the development of the PHITO cover concept. These vegetated boxes are two years old and have been outdoors for two winters.

Although the experiments are very preliminary, the results indicate that, after two years of freezing and thawing, the tailings have not acidified. These results support the literature, and the overall concept of an acid inhibiting PHITO cover.

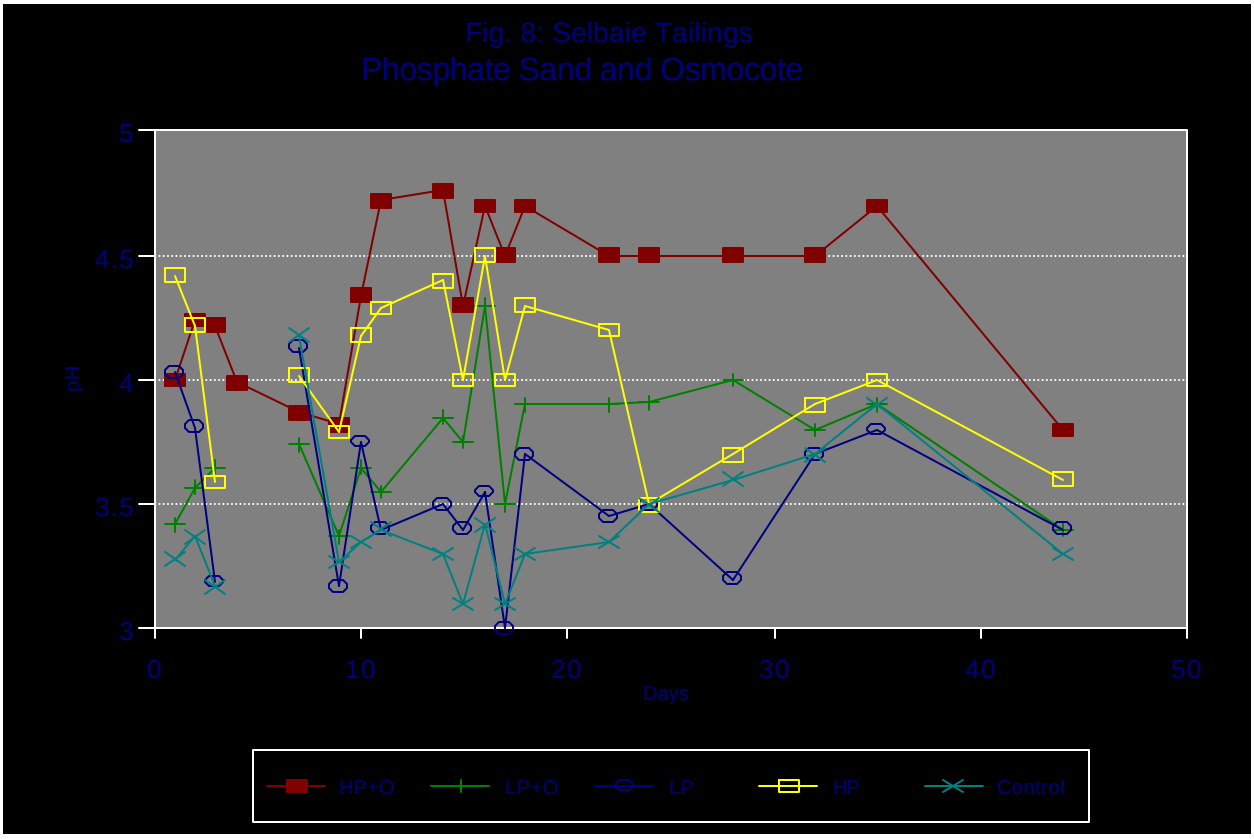


Table 9: Selbaie Tailings Vegetation Experimental Results, Spring 1991 - Spring 1993

		A	B	C	D	Control 1	Control 2
No Veg	pH	6.69	7.07	7.49	7.41	3.8	3.93
	Acidity	23.76	23.25	13.86	21.42	5551.9	10003.6
With Veg	pH	7.41	6.82	7.34	7.34		
	Acidity	11.52	29.52	26.25	189		
Kiddy pool	pH	5.5	5.42	5.96			
	Acidity	95.04	91.76	50.84			

INCO 1993

THE PHITO LAYER

SET-UP OF THE FIELD EXPERIMENT ON COPPERCLIFF TAILINGS

July 14 - 16, 1993

A. Fyson and M.P. Smith

INTRODUCTION: Application of phosphate rock to fresh tailings, combined with an active heterotrophic bacterial community, maintained by organic matter added as amendment and from a plant cover, should significantly reduce net acid release in the long term. An experimental plot was set up between July 14 and 16 on the Coppercliff tailings, on a 0.35 - 8 m thick pad of fresh tailings trucked to an old pyrrhotite tailings deposit. Phosphate rock, at two application rates, and partially decomposed horse manure, at two application rates were applied in the plot.

OBJECTIVE: To assess whether the combined effects of phosphate rock and heterotrophic activity significantly reduce acid generation rates following deposition of fresh tailings.

METHODS: Approximately 3000 m^3 of recently discharged tailings (4112 t, at moist density=1.36) were trucked onto a pyrrhotite tailings area and spread over an quasi-rectangular area approximately 70 m by 65 m in a 4 day period. The average thickness of the fresh tailings area is approximately 0.66 m (n=18), but ranges from 0.38 m to 0.84 m. There is a slope of 1-2 % from north to south accross the plots area slopes from north to south, at approximately a 1% to 2% slope.

Within this area, a rectangular plot 45 m x 51 m was staked out, such that the plot was 2 to 5 m from the edge of the tailings area. This plot was subdivided into 27 treatment plots numbered 1 through 27, arranged in a 3 x 9 lay-out, where each experimental plot is 15 m by 5.7 m.

Phosphate Rock Addition: Phosphate rock was spread using a PTO driven fertilizer spreader pulled by a tractor. Experimental plots 1 through 9 did not receive any phosphate rock. Plots 10 through 18 received the low application (3 kg/m^2) of phosphate rock, while plots 19 through 27 received the high application (30 kg/m^2) of phosphate rock. In this way, the two levels of phosphate were added parallel to the elevation gradient. This gradient has the potential to create a moisture gradient over the experimental area from plot 1 (driest) to plot 27 (wettest).

Horse Manure Addition: Horse manure was spread using the same set-up employed for the phosphate rock spreading. A low application (1.6 L/m^2) of horse manure was added to three strips (plots 2, 11 and 20, plots 5, 14 and 23, and plots 8, 17 and 26). A high application of horse manure was added to three strips, comprised of plots 3, 12 and 21, plots 4, 13 and 22, and plots 9, 18 and 27. No horse manure was applied to the other plots (plots 1, 10 and 19, plots 6, 15 and 24, and plots 7, 16, and 25).

In summary, plots with nine combinations of phosphate rock and horse manure were set up on the highest ground, intermediate ground and the lowest ground.

Mixing of Phosphate Rock and Horse Manure With Tailings: A PTO powered rotary tiller was used to till all 27 plots to a depth of 10 cm. Following tilling, the phosphate rock and horse manure appeared to be well mixed with the top 10-12 cm of tailings.

Dust Control: Using a hydroseeder truck, water was sprayed over the entire plot as a temporary dust control measure. This procedure wetted the surface 2-5 mm of tailings and effectively controlled wind-blow.

Seeding: Rye seeds were scattered over all plots using a seeder mounted on a tractor.

Sampling Tailings Material: Eighteen (18) holes were dug by hand in those plots marked in the attached schematic. The depth of fresh tailings was recorded. The excavated tailings were homogenized by hand and 400 cm^3 were collected in whirl-packs.

Installation of Leachate Collection Devices (LCDs): Eighteen (18) LCDs were built on site. The devices are designed as shown in Schematic 2. Holes were excavated at the centre of each of 18 plots, and the LCDs placed in the bottom. The holes were carefully backfilled by hand in order that the tailings were well compacted around the devices. Tubes leading from the devices were buried 0.25 m below the surface, but an attached yellow polypropylene rope was left to emerge from the top of the tailings when backfilling was complete. In this way, the location of the LCDs was marked such that tubing could be relocated and brought to the surface, once damaging surface activities such as rotary tilling were complete.

REQUIRED WORK REMAINING:

1) Seeding by Seed Drill: Only a sparse application of rye was scattered over the surface. In addition, seeding, using a seed drill, of the standard mix of seeds used by the Inco agricultural department should be performed at a rate of 100 lbs per acre as soon as possible.

Caution should be taken while drilling such that the plastic sampling lines of the LCDs are not pulled from the ground or cut up.

2) Stabilization of Peripheral Fresh Tailings Embankment: In their current condition, the edge of the plots, as well as the embankments, will very likely be eroded by wind and precipitation run-off. Therefore, crimping of straw into these surfaces should be performed as soon as possible to prevent erosion and dust problems.

MONITORING AND SAMPLING:

The plot will be sampled on three occasions in 1993 with tasks as follows:

1) 3-4 weeks after establishment (early August)
-assessment of vegetation establishment. Germination of rye and other species will be assessed. Height of rye seedlings will also be measured and the general appearance of the seedlings described.
-collection of leachate from LCSs and determination of water chemistry
-tailings pore gas composition
-tailings permeability

2) 7-8 weeks after establishment (early September) when the effects of the various treatments should be apparent

-assessment of vegetation
-assessment of oxidation under various treatments (core samples of tailings-determination of acidity, conductivity, pH, iron and sulphate of pore water and sulphide content of tailings)
-quantification of leachate from LCSs and determination of water chemistry)
-tailings pore gas composition
-tailings permeability

3) 11-12 weeks after establishment (October), at the end of the growing season

-collection of tailings cores
-determination of above and below ground biomass and root distribution,
-distribution of oxidation zones
-enumeration of heterotrophs and oxidising bacteria (thiobacilli)
-pore water chemistry
-leachate quantity and chemistry (LCSs)
-tailings pore gas composition
-tailings permeability

DENISON 1993

DEVELOPMENT OF THE PHITO COVER FOR THE STANROCK TAILINGS

Report on field trip of 24-27 August 1993

The overall objective of setting up a field plot for demonstration of the effectiveness of a phosphate rock-heterotrophic bacteria "biolayer" on the Stanrock tailings was achieved

Site Selection

A reconnaissance was made over the tailings to select an experimental plot which met the following criteria:

1) Accessible
2) Representative
3) Lime free
4) Workable surface (with rotary tiller)
5) Homogeneous (flat, equally oxidised, lacking in runoff channels etc.)
6) Sufficiently large to determine the effectiveness of the treatments

The selected area was the only place which met most of these criteria. The area is essentially free of visible lime on the surface, is fairly flat and with only one or two trees and a little grass (the presence of these indicates the capacity for the site to support vegetation). This vegetation was removed prior to setting up the experiment. The chosen plot was 33 m x 36 m and was divided into the 27 sub-plots shown in the schematics in the proposal (see also Schematic 1). The scale of the plot is somewhere between the 'hand' sown and 'mechanically' sown versions shown before. The sub-plots are 4 m x 11 m, sufficient for establishment of conditions with small overall edge effects. The phosphate rock and horse manure were tipped onto the plots from a trailer and worked in to the surface (to 10 cm depth) with a rotary tiller.

All plants were sown with a grass-legume mix with the following composition:

This mix is designed to assure a good cover under a wide range of conditions. The plots were also sown with winter rye. The seed was spread by hand. A 3 m strip was left at the end of each of the three phosphate treatments in order to determine the effect of vegetation on the tailings.

'Mushroom' water collectors were placed in 9 plots (1 of each treatment). A hole was dug to 73-81 cm depth and the water collector placed in position, the tailings were then returned carefully to the hole, to ensure that oxidised, surface tailings were replaced at the surface. The structure and functioning of theses devices are shown in Schematic 2. The screen of the water collectors was located at a depth of 50 to 55 cm. These devices have been designed to collect water passing through the tailings column, to determine the effect of the various treatments on water leaching through the tailings.

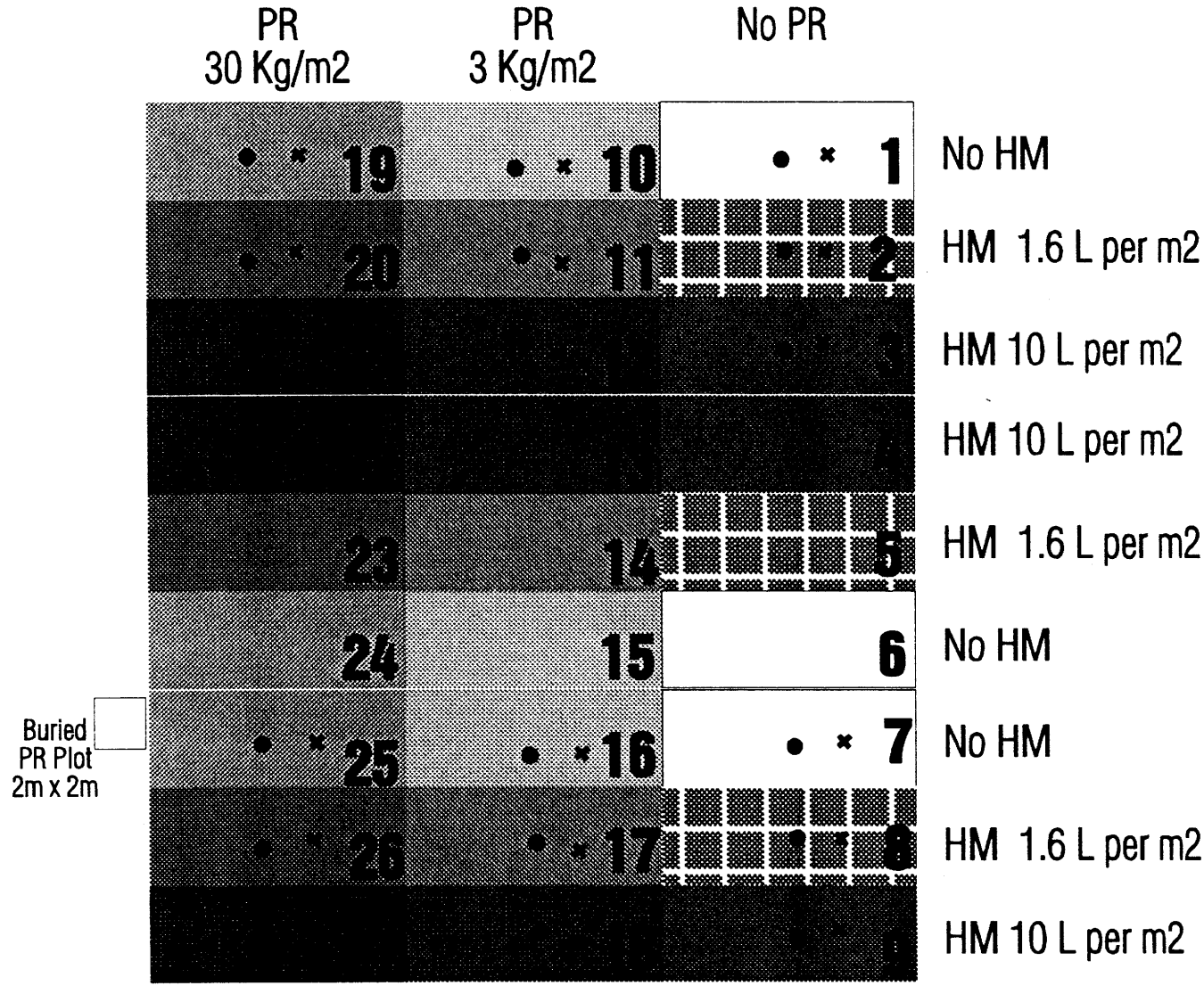
Tailings profiles showed three distinct colour zones, orange, pale grey and dark blue-grey. The distribution of these zones in holes dug for the water collectors are shown in Table 1. Samples were taken from these holes. These will provide baseline chemistry data for the later determination of treatment effects. Slurries of these tailings will be made and sampled to determine titratable acidity/alkalinity, pH etc.

The site will be visited approximately two weeks after sowing to determine whether adequate germination has taken place. If not, the plots will be resown. At this time, the water collectors will also be sampled.

Table 1 Tailings profiles, August 24, 1993
Appearence of tailings in walls of holes dug for placement of water collectors

Plot #	Total depth (cm)	Orange zone (cm)	Pale grey zone (cm)	Blue grey zone (cm)
4	74	0-45	45-59	59+
5	81	0-40	40-52	52+
6	73	0-27	27-43	43+
13	81	0-32	32-49	49+
14	73	0-31	31-55	55+
15	77	0-50	none	50+
22	80	0-25	25-46	46+
23	81	0-32	32-60	60+
24	80	0-30	30-48	48+

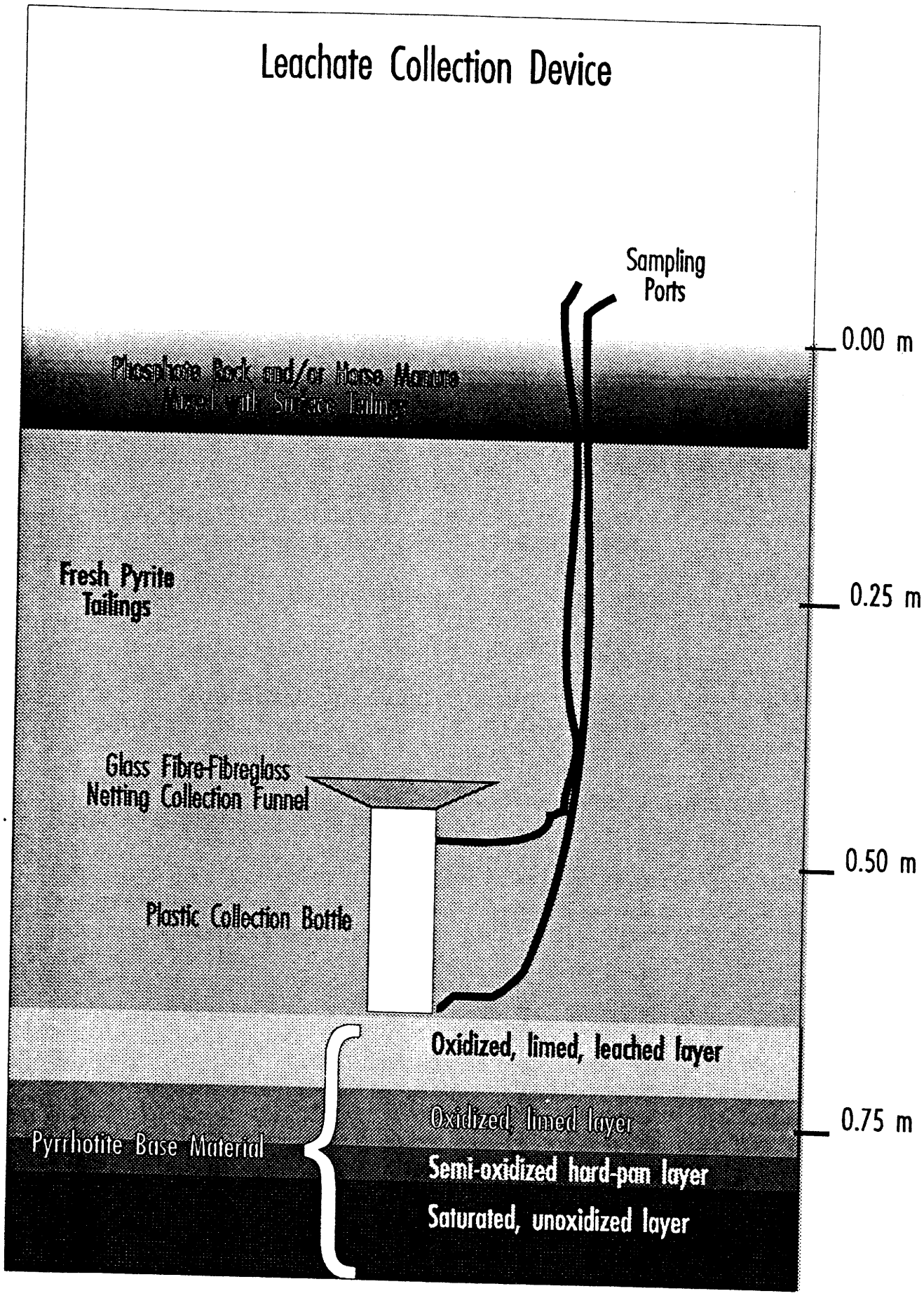
Incl 1.



✖ Tailings Sample and Total Depth Measurement

● Location of Leachate Collection Device

Schem. 2


Leachate Collection Device
Sampling Ports
0.00 m
Phosphate Rock and/or Horse Manure
Mixed with Surface Tailings
Fresh Pyrite Tailings
0.25 m
Glass Fibre-Fibreglass Netting Collection Funnel
0.50 m
Plastic Collection Bottle
Oxidized, limed, leached layer
Oxidized, limed layer
0.75 m
Pyrrhotite Base Material
Semi-oxidized hard-pan layer
Saturated, unoxidized layer

APPENDIX 4

PHITO MONITORING PROGRAM PROPOSAL-MEND 1994

TECHNOLOGY INFORMATION SHEETS

ZENECA PROPOSAL FOR IWP-JULY 1994

Brunswick Mining and Smelting
Corporation Limited
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Bathurst, New Brunswick E2A 3Z8

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brunswick

1994 05 16

1100-7

Dr. M. Kalin
Boojum Research Limited
468 Queen Street East, Suite 400, Box 19
Toronto, Ontario
M5A 1T7

Dear Margarete:

Thank you for providing information and experimental data concerning your proposal for use of phosphate in a variety of dry cover configurations, and in particular the PHITO cover. You are of course correct: I am the lucky one who will formulate a dry cover program for consideration by the MEND Program Prevention and Control Committee. You are mistaken concerning the timing, however, as I will outline and distribute a proposed program in June. Additional MEND funding will not be approved prior to the next fiscal year and any projects that do proceed would most likely be associate projects that could be considered again in future for acceptance as full MEND projects. The committee will not meet until September, although we will discuss my proposal by telephone before that time.

Unfortunately I will not be able to call you in the near future but I will do so in late May or early June. In the interim I must concentrate on more immediate priorities including a directors meeting, annual meeting of shareholders, briefing of our incoming president and another week of campaigning for industry through the Environmental Issues Group of the Whitehorse Mining Initiative.

Thank you for your interest and understanding. I look forward to speaking with you soon.

Yours truly,

L.J. Surges
Director, Environment

c: **G. Tremblay**

Boojum RESEARCH LIMITED
468 Queen St. East, Ste. 400, Box 19, Toronto, Ont. M5A 1T7 (416) 861-1086 Fax (416) 861-0634

May 13, 1994

Mr. Leonard Surges
Brunswick Mining & Smelting
PO Box 3000
Bathurst, NB
E2A 328

Dear Leonard:

In assessing where my long standing PHITO cover proposal stands with the MEND committee, I was informed by Gilles Tremblay, that you are the lucky one, who has to consider dry covers and research in this area.

Since Inco and Denison have installed the plots last year, and Boojum has done the background work of phase I and II in anticipation of the review of the dry cover technologies which was under way at the time (SENES study), monitoring of the plots for 1993 should commence.

I would like to discuss with you the background of this work prior to your anticipated MEND meeting, which is apparently forthcoming. I would appreciate a call at your earliest convenience. I attach for your information one sheet of results obtained with base metal waste rock and NPR after rock has been outside for two winters.
The inhibition noted from the experiment is rather impressive.

Yours sincerely

Margarete Kalin

enc. Proposal PHITO and results Phosphate rock

1.0 PROPOSAL TO START MONITORING THE PHOSPHATE HETEROTROPH INHIBITION OF TAILINGS OXIDATION

1.1 Background

Phosphate rock and an appropriate organic carbon source, along with a vegetation cover, provides:

- secondary mineral formation on and within the tailings particle matrix, which reduces the permeability of the tailings and reduces access of oxygen to pyrite particles;
- oxygen depletion, due to the growth of heterotroph microbial communities, which reduce the activity of oxidizing bacteria such as *Thiobacillus*.

The Phosphate Heterotroph Inhibition of Tailings Oxidation (PHITO) cover will operate in the long term as a terrestrial ecosystem, where plants and phosphate rock interact to favour the growth of oxygen-consuming, heterotrophic bacteria. Phosphate rock acts as a fertilizer and as an acidity neutralizer. Several processes work concurrently within the inhibitory cover:

- geochemical interactions between tailings and phosphate rock - acidity neutralization;
- secondary mineralization on pyrite surfaces in the vadose zone - phosphate precipitates create an low permeability layer, which blocks the movement of oxygen and water thereby slowing the oxidation of sulphide minerals;
- as well as neutralizing the tailings, phosphate rock is a nutrient source for the germination and growth of vegetation cover;
- microbial community development.
- self-sustaining nutrient cycle - phosphorus taken up by plants remains in the soil and provides nutrient for subsequent generations - further phosphate applications should not be necessary.

The rate of population growth of these bacteria is considerably higher than that of *Thiobacillus*. The aerobic bacteria, and the cattail roots take up a significant amount of oxygen from the water, thereby suppressing *Thiobacillus* activity and acid generation.

As part of the federal MEND program, Boojum initiated a three phase program:

Phase I: background review of phosphate rock chemistry to provide parameters for the design of test plots at Copper Cliff and Elliot Lake.

Phase II: test plots were established on Copper Cliff and Denison (Stanrock) tailings. Phosphate sand, and manure were harrowed into the top 15 cm of the tailings. Grass seeds germinated, grew and overwintered. Seepage was collected from one meter below the surface only on the Denison tailings.

Phase III: monitoring and quantifying the effectiveness of the cover. This phase was scheduled to begin in 1994 and be completed by 1996.

At the end of Phase III, it should be possible to establish reliable design criteria for optimal performance: the rate of phosphate utilization, and the degree of AMD inhibition.

Phases I and II have been completed. However, MEND program funding of Phase II (1993 activities) and Phase III has not been given to date. Since PHITO plots were successfully established, a re-evaluation of the proposal is requested. Boojum strongly believes that it is very worthwhile completing this project.

1.2 Scope for Phase III, Two Years: 1994 and 1995

The following activities are proposed during each of the next two years:

- Boojum will prepare a protocol for sampling seepage collecting in the "mushrooms" installed under the test plots and from the control area;
- Boojum personnel will collect and analyze (pH, redox measurements and acidity titrations) the water samples;
- Boojum personnel will take root zone samples and measure plant growth and bacteria populations.
- Boojum will prepare an interim report at the end of 1994.
- With the data at hand, a GO/NO GO is anticipated for confirmation in 1995.

Deliverables: A 1994 final report, including an estimate of the cost of installing and maintaining PHITO on a large scale will be issued to allow GO/NO GO.

1.3 Costs

The cost estimate for Boojum's services for the first year (1994) is shown on the attached spreadsheet. These are based on 1994 charge-out rates for Boojum personnel, see attaches Schedule 1. Costs incurred for plot maintenance and analysis for metal loadings in the water (by INCO) have not been included.

The total cost of services billed in 1994 will not exceed $ 19,500 without prior authorization. Costs for the next year will be based on 1995 charge-out rates and prices, and any scope changes: a budget will be presented at the end of 1994, with the interim report.

inco wk1

COPPER CLIFF TAILINGS PHITO PROJECT - 1994 BUDGET SUMMARY

A. LABOUR							TOTAL	COST
PERSONNEL	M. Kalin	C.Farrow	M. Smith A.Fyson	J.Y. Liu	M. Wanat	M English	DAYS	
RATE	$650	$600	$450	$450	$300	$300		
1. Field Work								
2 site visits x 3 days			3		3	6	12	$4 050
2. Laboratory Work					5		5	$1 500
3. Data Interpretation & Summary								
Sampling protocol			1				1	$450
4. Report Writing			6				6	$2,700
5. Project Management	1	2					3	$1 850
TOTAL LABOUR						TOTAL LABOUR	27	$10,550

B. CONSUMABLES		
1. Allowance for acidity titrations, bioassays etc		$2 000
Chemical analysis of water samples		by INCO
2. Laboratory equipment use at $ 400/lab technician day		$2 000
3. Field Equipment and Supplies		
	TOTAL LAB/FIELD EXPENSES	$4 000
C. ADD 30% G&A ON LABOUR	30% G and A ON LABOUR	$3 165
D. TRAVEL AND ACCOMMODATION		
Transportation - car @ $0 32/km		
2 trips x 950 km/trip		$600
Food and Accommodation		
2 trips x 2 persons x 3 days x $100/day		$1 200
	TOTAL OTHER EXPENSES	$1 800
	TOTAL PROJECT COST	$19,515

TRANSMISSION REPORT

TIME : MAY 16 '94 11:33
TEL NUMBER : 4168610634
NAME : BOOJUM RESEARCH LTD.

NBR	CARD#	FILE	DATE	TIME	DURATION	PGS	TO	MODE		STATUS	
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BOOJUM RESEARCH LIMITED
BOOJUM TECHNOLOGIES

USES OF NATURAL PHOSPHATE ROCK

Natural phosphate sand (NPR) can be used in a number of ways:

- to reduce acidity and precipitate iron by addition to strongly acidic water.
- to form insoluble, low permeability layers in fresh tailings. In conjunction with a vegetation cover with oxygen consuming bacteria populations in the root zone, NPR integrated into the tailings vadose zone may provide a stable cover, reducing the rate of acid generation.
- phosphate rock spread in layers as acid generating waste dumps are constructed, iron will precipitate on the acid producing mineral surfaces and form barriers, which inhibit further oxidation, thereby decreasing the amount of acid generated.
- as a nutrient for biological polishing systems.

Processes

IWP (Inhibit With Phosphate)

PHITO (Phosphate Heterotroph Inhibition of Oxidation)

PWP (Precipitate With Phosphate)

For more information, contact: M. Kalin, Boojum Technologies Ltd., 468 Queen St. E., Suite 400, Toronto, Ontario, Canada M5A 1T7 (416) 861-1086; fax (416) 861-0634

BOOJUM RESEARCH LIMITED
BOOJUM TECHNOLOGIES

PHITO (Phosphate Heterotroph Inhibition of Tailings Oxidation)

Phosphate rock and an appropriate organic carbon source, along with a vegetation cover, provides:

- secondary mineral formation on and within the tailings particle matrix, which reduces the permeability of the tailings and reduces access of oxygen to pyrite surfaces.
- oxygen depletion, due to the growth of heterotroph microbial communities, which reduce the activity of oxidizing bacteria such as *Thiobacillus*.

The PHITO cover will operate in the long term as a terrestrial ecosystem, where plants and phosphate rock interact to favour the growth of oxygen-consuming, heterotrophic bacteria. Phosphate rock acts as a fertilizer and as an acidity neutralizer. Several processes work concurrently within the inhibitory cover.

- geochemical interactions between tailings and phosphate rock - acidity neutralization.
- effects of secondary mineralization on vadose zone behaviour - phosphate precipitates reduce permeability, which reduces the movement of water thereby slowing the oxidation of sulphide minerals.
- as well as neutralizing the tailings, phosphate rock is a nutrient source for the germination and growth of vegetation cover.
- microbial community development.
- self-sustaining nutrient cycle - phosphorus taken up by plants remains in the soil and provides nutrient for subsequent generations - further phosphate applications should not be necessary.

Applications: PHITO covers are being tested on "fresh" (recently deposited) and weathered tailings. Plots have to be monitored for several years before the effectiveness can be determined.

For more information, contact: M. Kalin, Boojum Technologies Ltd., 468 Queen St. E., Suite 400, Toronto, Ontario, Canada M5A 1T7, (416) 861 1086; fax (416) 861 0634

BOOJUM RESEARCH LIMITED
BOOJUM TECHNOLOGIES

PWP PROCESS (Precipitation With Phosphate)

Strongly acidic waste water has to be treated before biological processes can be expected to work. The PWP process uses crushed phosphate (apatite) rock. Phosphate rock has a number of advantages over other chemical treatment, in that it buffers, forms a dense, insoluble precipitate, and provides nutrients to subsequent biological processes.

Test Results to Date:

- Waste rock pile seepage: a field test was performed to remove ferric iron from waste dump acid seepage, pH 2 to 3.5, improving the quality of water flowing to the subsequent ARUM and biological polishing stages.

  Seepage flowed through an NPR drain. On average, the iron concentrations fell from about 1500 mg/L in the feed water to about 560 mg/L; $CaCO_3$ acidity was reduced by about 35%, which was sufficient to get biological polishing established.

- Coal seepage: a field test was performed to remove ferric iron from an acidic coal seepage, pH 3.5 improving the quality of water before passing through a wetland.

  Seepage flowed through two phosphate rock berms. On average, the iron concentrations dropped from 169 mg/L to 64 mg/L: CaCO3 acidity was reduced by approximately 25%.

For more information, contact: M. Kalin, Boojum Technologies Ltd., 468 Queen St. E., Suite 400, Toronto, Ontario, Canada M5A 1T7 (416) 861-1086; fax (416) 861-0634

IWP Process (Inhibit With Phosphate)

The IWP Process is being developed for inhibition/reduction of acid generation in waste rock piles. The results of an outdoor experiment using base metal waste rock exposed over two winters are outlined below:

Accumulated acidity after 574 days (March 22, 1994)

			Acidity (g)	% inhibition
A1	low pyrite fresh	control	57.1	
A2		+PR mixed	2.6	95
A3		+PR layer	3.2	94
B1	high pyrite fresh	control	60.4	
B2		+PR mixed	3.0	94
B3		+PR layer	4.1	92
C1	low pyrite	control	153.9	
c2	>4 yr exposure	+PR mixed	11.6	92
C3		+ PR layer	29.8	81
E1	high pyrite	control	24.2	
E2	>4 yr exposure	+PR mixed	2.0	92
E3		+PR layer	34.5	-43

For more information, contact: M. Kalin, Boojum Technologies Ltd., 468 Queen St. E., Suite 400, Toronto, Ontario, Canada M5A 1T7 (416) 861-1086; fax (416) 861-0634

IWP - Inhibition With Phosphate

Phase I 1992-1994 Summary
Phase II Sept 1994 - March 1996

1. PHASE I: SUMMARY

Oxidation of pyrite in mining wastes results in metal-laden acidic waters. Oxidation is mediated by weathering (chemical oxidation) and microbial action. The pyrite surface, where oxidation occurs is a target for preventive measures.

The conditions which will lead to coating of the mineral surface are those which are undesirable in metal leach piles. A copper leach pile in British Columbia stopped producing copper. Rocks from within the pile were obtained and found to be heavily coated with secondary minerals. Electron microscopy/electron dispersive spectroscopy (EDS) investigations of the surfaces indicated the presence of phosphates.

An experiment was set up at the Boojum facility, in which pyritic waste rock is weathered (oxidised) in the presence or absence of a phosphate rock mineral (small gravel size). Waste rocks were placed in 70 L drums in ambient climatic conditions. Rocks of 4 types were tested, previously exposed to differing periods of weathering and containing different amounts of pyrite. Phosphate rock was added to some drums either mixed throughout the drum or confined to a layer to the top half of the drum. In addition, thin sections of rocks on microscope slides and polished cut rocks were placed in the drums. Half of each cut rock was stored under conditions (nitrogen gas) where oxidation can not occur. This will allow for determination of effects of oxidising conditions on the rock surfaces.

The first phase of the experiment was to monitor the acid generated from the drums. The results to date are summarized in the attached plots of acidity, accumulated over 678 days, or nearly two complete years. The accumulated acidity measurements and the effects of phosphate rock are summarised in Table 1.

Placement of phosphate rock throughout the drums resulted in >90 % reduction in acid generation over the study period. With the exception of the high pyrite, previously weathered rock (E drums), incorporation of phosphate rock in the top of the drum alone also resulted in a substantial reduction (>80 %) of accumulated acid generation. The seasonal behaviour of the acid generation process are given for all the treatments in Figures 1-4. The differing behaviour of the E3 drum with acidity peaks in the winter months has not yet been explained.

2. PHASE II SCOPE OF WORK

The drums require dismantling for examination of the waste rock surfaces to define the conditions associated with the inhibition in acid generation.

Chemical analysis must be carried out on the effluents from the drums collected over a 678 day period and stored in the refrigerator. The secondary precipitates must be identified and related to the presence of phosphate rock. Rainfall has been measured and the rain water has collected and stored. A control drum (phosphate rock alone, no pyrite waste) is part of the experiment and has been monitored.

Some initial background scanning electron microscopy/EDS investigations have been carried out, reports of which are with ZENECA. These studies confirmed the presence of secondary precipitates, and provided visual evidence of pyrite oxidation. This work should be continued to determine the relationship between phosphate rock, secondary precipitates and bacteria on the inhibition of oxidation.

Some initial experimental work has been carried out to investigate the colonization of the waste rock surfaces by oxidising bacteria. Scrapings from pyrite surfaces of rocks extracted from the drums were incubated in media for oxidising bacteria (*Thiobacillus* spp.). After two or three weeks bacteria were observed in the media and visual evidence of oxidation of Fe(II) in the medium was observed. The distribution of such bacteria in relation to other observations such as the presence of characterised secondary precipitates is needed to establish the effect of such materials on bacterially mediated oxidation.

3. LOGISTICS AND COST ESTIMATE

It is proposed that Phase II is to be continued with Professor Grant Ferris, in the Department of Geology, University of Toronto. Professor Ferris has considerable expertise in microbial mediated secondary mineral formation and the application of quantitative electron microscopy techniques to identify mineral forms associated with particular surfaces. Boojum Research is down-sizing but would maintain involvement in the project. Through the transfer of the work to the University it might be possible to obtain funding through the National Research Council. The project's first phase had support from the National Research Council of Canada (NRC). Such NRC funding requires 50 % support from industry which was provided by Inco, Denison Mines and Boojum Research. The experiment was initiated while Boojum was under contract with Shell International. All the results to date belong to Boojum Research.

It is requested that ZENECA would consider becoming the industrial partner or sole contractor for Phase II of the experiment. It is possible to seek joint funding under the Natural Sciences and Engineering Research Council (NSERC, fax sent July 11, 94), as the major part of Phase II would be university-based.

A preliminary cost estimate of Phase II has been arrived at, $180,000 over a period of 18 months. This budget consist of cost of a research assistant's time, the time of Professor Ferris time, electron microscopy/EDS, chemical and microbial analysis of the rock surfaces following disassembly of the drums, which would be carried out by Boojum Research.

Table 1: Accumulated acidity after 678 days (to July 4, 1994)

Drum	Rock type	Treatment	Acidity (g)	Inhibition (%)
A1	low pyrite	control	62	
A2	fresh	+ PR mixed	3	95
A3		+ PR layer	4	94
B1	high pyrite	control	55	
B2	fresh	+ PR mixed	3	95
B3		+ PR layer	7	87
C1	low pyrite	control	166	
C2	>4 y weathering	+ PR mixed	12	93
C3		+ PR layer	33	80
E1	high pyrite	control	26	
E2	>4 y weathering	+ PR mixed	2	93
E3		+ PR layer	40	-52

Fig. 1: Acidity-Drums A1-A3
Low Pyrite 'Fresh'

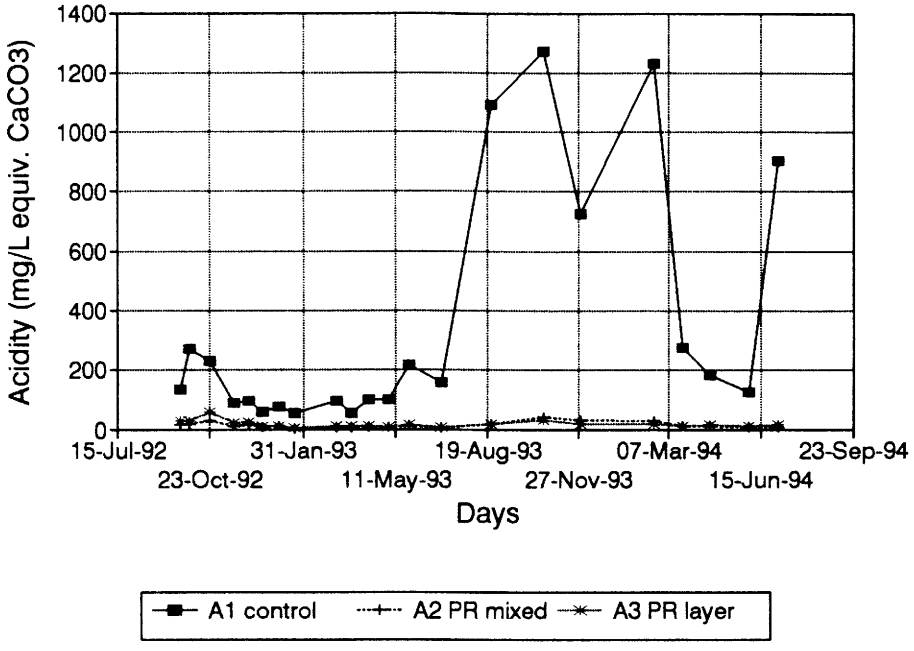

Fig. 2: Acidity-Drums B1-B3
High Pyrite 'Fresh'

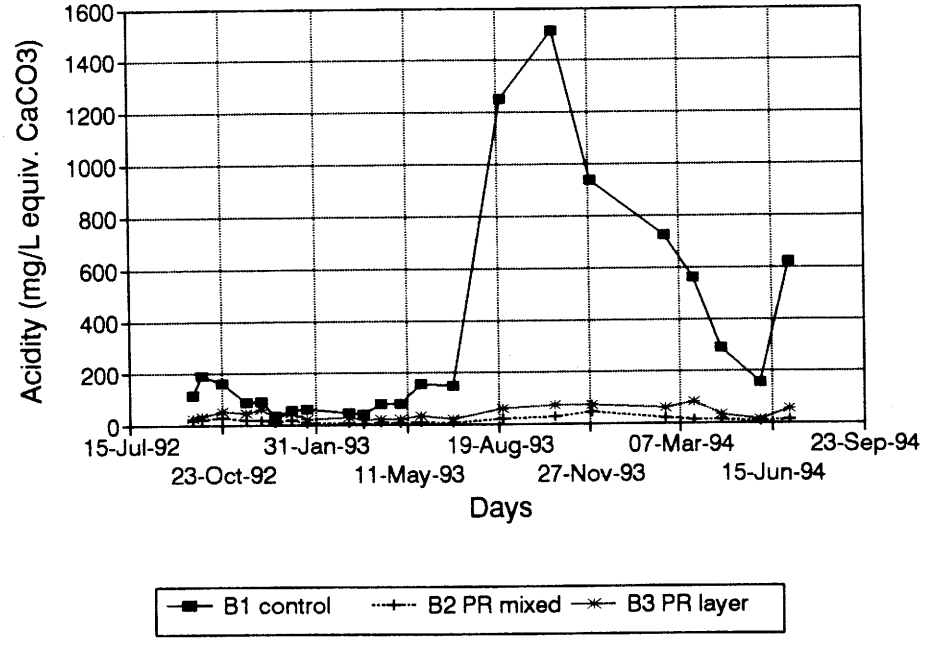

Fig. 3: Acidity-Drums C1-C3
Low Pyrite 'Weathered'

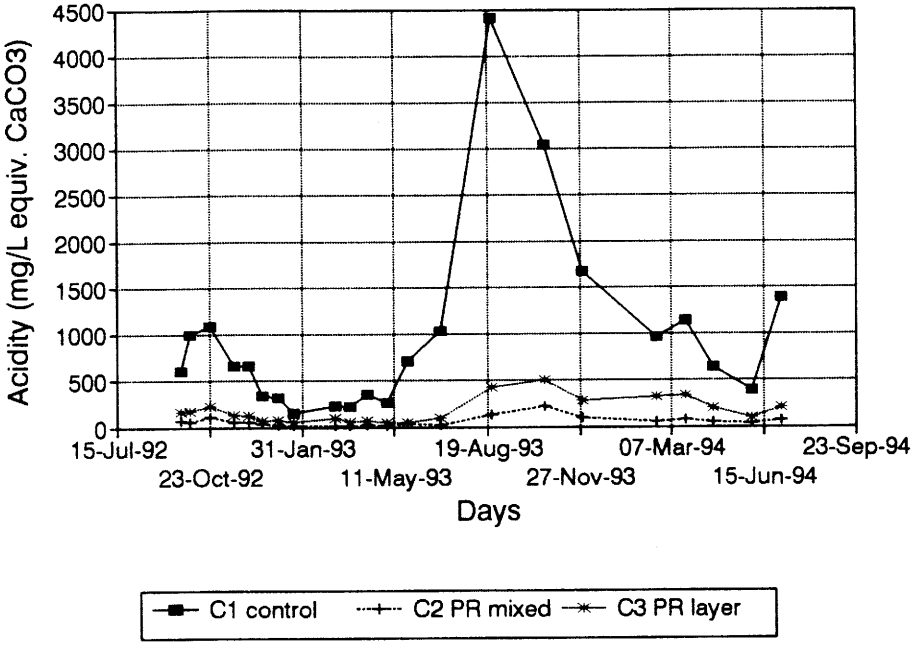

Fig. 4: Acidity-Drums E1-E3
High Pyrite 'Weathered'